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# DOUBLE GROUPS AS SYMMETRY GROUPS FOR SPIN-ORBIT COUPLING HAMILTONIANS

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**ABSTRACT.**

The present notes endeavour, in what is believed to be a rather new approach, to give a precise definition of double groups of proper and improper point groups and a precise description of the mathematics of their application as symmetry groups for certain classes of molecular electronic Hamiltonians containing a spin-orbit coupling term. The ambiguities and mysticism traditionally associated with the double groups is removed by, firstly, defining the double groups of proper point groups as subgroups of SU(2) [thus following Opechowski] rather than by the "addition" of a phantom non-identity $2\pi$ rotation and, secondly, establishing in a rigourous way the connection between the double groups and the operators mentioned. The latter is achieved by emphasizing the concept of operator representations of a group.

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Contents

## 1. Introduction.

Since the appearance of the famous "Termaufspaltung" paper by Bethe [1], chemists and physicists have used the double groups of the ordinary point groups in their symmetry analysis of electronic Hamiltonians containing a spin-orbit coupling term. A vast standard literature is available describing the mathematics of the double groups in general [e.g., 2-12] or just that of their common supergroup, the full rotation double group [e.g., 13-16]. Some recent papers are concerned with definitions of the double groups in the context of so-called projective representations [17-19 and references in these]. However, when it comes to the problem of explaining why the double groups turn up in certain chemical or physical situations, many texts start discussing intricate questions such as the possible distinguishability for fermion wavefunctions of $2\pi$ and $4\pi$ rotations, intrinsic "parity" of electrons, etc. Such approaches may, indeed, have their merits from the point of view of obtaining a physical feeling for the situations where double groups arise, but they tend to impair a certain measure of mysticism and, consequently, vagueness to the definition of the double groups themselves. This may give rise to problems when the double groups are to be used for detailed quantitative analyses.*)

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*) This is not to say that these physical aspects are not of importance. On the contrary, consider the recent experimental work aiming at confirming the $4\pi$ (but not $2\pi$) periodicity of fermion wavefunctions [20]; see also discussions of analogous phenomena in macroscopic geometry [21]. The point is just that we are able to avoid basing our definition of double groups on such speculations.

Strangely, no texts known by the present author - with the partial exception of [4] - proceed simply by establishing the double groups as symmetry groups for the spin-orbit coupling Hamiltonian, i.e., as groups representable by groups of operators which commute with this Hamiltonian. If, however, one does adopt this line of thought, one has the mental advantage that any more or less transparent physical arguments only enter the discussion through the assumption of a particular Hamiltonian, whereas the introduction of the double groups may be accomplished separately with complete rigor.

On this background, the major purpose of these notes is to show how the symmetry-group viewpoint may lead to the double groups and, in fact, to the concrete matrix realization discussed by Opechowski [2] which is well suited for a precise mathematical description.

We start by stressing in Chapter 2 the fact that a group used for symmetry analysis of an operator acting on some space may be of any particular abstract or concrete kind, provided that it is connected to the operator by a suitable operator representation of the group on that same space. This point of view is crucial to the subsequent introduction of double groups as matrix groups.

Chapter 3 describes the type of model Hamiltonians to be investigated. The central Chapter 4 then presents a thorough discussion of the way the double groups may be used as symmetry groups for such Hamiltonians. Note in particular that double groups of improper point groups are also defined. Chapter 5 gives some of the group theory of the double groups thus introduced, and Chapter 6 contains some remarks on the actual application of them. In Chapter 7 we collect a few additional comments; it may be of interest to note already here that the historical remarks trace the double groups back to the middle of the last century, long before the appearance of Bethe's paper.

Some mathematical material, mainly proofs of assertions made in the main text, has been put in the appendix to facilitate reading of the main text.

The reader who wishes to follow the arguments of these notes closely will need familiarity with the following mathematical material: basic notions of operators on linear and Hilbert spaces; basic definitions of group theory (group, homomorphism, ordinary matrix and operator representations of groups, direct product of groups); and the concept of tensor products (direct or Kronecker products) of linear spaces, of operators, and of group representations, for all of which we shall use the product symbol "$\otimes$". We shall not be concerned with the aspects connected with projective representations (for this, see the references cited above).

## 2. Group representation analysis of operators; symmetry groups.

The present chapter describes the mathematical features of one of the general situations in which group representations are in an interplay with a (quantum-mechanical) model operator being studied. The purpose at this stage is not to introduce any new mathematics, but rather to emphasize a point of view which the author has found generally useful and which will, in particular, be invoked in the presentation of double groups later on in these notes.

Suppose that we are studying some operator $\mathcal{H}$ acting on a finite-dimensional Hilbert space V.

The symbol $\mathcal{H}$ is of course reminiscent of "Hamiltonian", but we make no assumptions here regarding the nature of $\mathcal{H}$. The assumption that V is finite-dimensional is made to avoid in the sequel a series of technical mathematical comments and digressions which would just obscure the ideas to be presented. In most of the practical applications we are aiming at, only operators on finite-dimensional spaces are involved anyway.

Assume further that a pair $(G,\mathcal{T})$ is given, where G is a group and $\mathcal{T}$ a unitary operator representation of G on V. Thus, $\mathcal{T}(R)$ is a unitary operator on V for each $R \in G$ and the operators $\mathcal{T}(R)$ form a homomorphic image of G.

Since groups are often in applications of the present kind themselves thought of as having operators for their elements, it may be useful to consider in some detail an example of how one may have occasion to consider such operator representations of groups.

Suppose we choose a Cartesian coordinate system somewhere in 3-dimensional space and study some point group G realized as transformations that fix the origin of this coordinate system. Any group element $R \in G$ will have a definite action on vectors $\mathbf{r}$ so that a new vector $R\mathbf{r}$ results when applying R to $\mathbf{r}$.

Now assume that we are also studying a set of functions defined in our space - e.g., a set of p or d orbitals centered at the origin. The transformations R may also be made to act on such functions in the well-known way: given a function $\psi$, the transformed orbital $\psi_R$ is defined by

$$\psi_R(\mathbf{r}) = \psi(R^{-1}\mathbf{r}). \tag{2.1}$$

The operator mapping functions $\psi$ onto the corresponding functions $\psi_R$ is often also just denoted R. If one wishes to make a distinction, however, one may use a symbol like $\mathcal{P}_R$. If we do this, we have the situation that every group element R is assigned an operator $\mathcal{P}_R$ defined by

$$\mathcal{P}_R(\psi) = \psi_R \tag{2.2}$$

for all functions $\psi$ in the function space considered. Thanks to the particular form of definition (2.1), the mapping $R \to \mathcal{P}_R$ (which itself is denoted $\mathcal{P}$ without any subscript) is a homomorphism, i.e.,,

$$\mathcal{P}_{RS} = \mathcal{P}_R \mathcal{P}_S \quad \text{for all } R,S \in G, \tag{2.3}$$

and thus an operator representation of G. It is, in fact, also unitary. We thus have an example, namely $(G,\mathcal{P})$, of the kind of pair $(G,\mathcal{T})$ referred to above. (For a more thorough discussion of operators of the type $\mathcal{P}_R$, see, e.g., [9, Sec.3-6; 14, Chap.11; 22, Chap.XIII, §11].)

Speaking of representations, if we choose an orthonormal basis set of vectors in 3-dimensional space, any $R \in G$ will have an orthogonal 3×3 matrix $\mathbf{R}$ with respect to this basis. The mapping $R \to \mathbf{R}$ is clearly a homomorphism and thus a matrix representation of G. Since it is also faithful (one-to-one, injective), we may, in fact, identify G with the set of matrices $\mathbf{R}$, and this is the way we shall look at point groups in the remainder of these notes.

The representation $\mathcal{T}$ induces an action of G on the linear operators on V by the prescription

$$\mathcal{O} \rightarrow \mathcal{T}(R)\,\mathcal{O}\,\mathcal{T}(R)^{-1} \qquad (2.4)$$

for all $R \in G$ and all operators $\mathcal{O}$ on V.

The definition (2.4) represents the generalized "rotation of observables" corresponding to the generalized "rotation of state vectors" effected by the operators $\mathcal{T}(R)$, $R \in G$ (cf., e.g., [4, p.55; 22, Chap.XIII, §12]).

By an "analysis of the operator $\mathcal{H}$ on V with respect to $(G,\mathcal{T})$" we shall mean an examination of the decomposition of V into subspaces invariant and irreducible under $\mathcal{T}$ and of the behaviour of $\mathcal{H}$ under the operator action of $\mathcal{T}$ defined in (2.1). In the following, we shall often focus on the situation where $\mathcal{H}$ in this latter respect transforms under $\mathcal{T}$ as the totally symmetric irreducible representation:

$$\mathcal{T}(R)\mathcal{H}\mathcal{T}(R)^{-1} = \mathcal{H} \quad \text{for all } R \in G \qquad (2.5)$$

or, equivalently,

$$\mathcal{T}(R)\mathcal{H} = \mathcal{H}\,\mathcal{T}(R) \qquad \text{for all } R \in G. \qquad (2.6)$$

In this case, we shall say that $(G,\mathcal{T})$ is a symmetry group for $\mathcal{H}$.

Note the use of the indefinite article; there is in no way any uniqueness associated with the concept defined here, and we are in no conflict with definitions of "the symmetry group" of an operator given at various places in the literature.

Having a symmetry group is a desirable situation, giving the well-known advantage of being able, briefly stated, to completely or partly diagonalize $\mathcal{H}$ by adapting basis vectors in V to $(G,\mathcal{T})$. And even if one analyses with respect to a group which is not a symmetry group, useful information of a quantitative nature may be obtained by using the Wigner-Eckart theorem if certain suitable quantities associated with the group are available (*i.e.*, if the Wigner-Racah algebra of the group [14, 23, 24, 36] is sufficiently developed).

In much of what is written on the use of symmetry groups, the representation $\mathcal{T}$, which describes "how the group G acts on V", is not mentioned explicitly. Usually it is clear from the context what $\mathcal{T}$ is; furthermore $\mathcal{T}$ is usually a faithful (one-to-one, injective) representation, making it perfectly admissible to identify G with its image $\mathcal{T}(G) = \{\mathcal{T}(R) \mid R \in G\}$ under $\mathcal{T}$, so that G itself becomes a group of operators on V.

However, retaining the operator representation $\mathcal{T}$ in the description does give one the possibility of studying the group G separately, regarding it as an abstract group or realizing it in any concrete manner one may wish. There is then no restriction on the nature of the elements in G, since $\mathcal{T}$ takes the full responsibility for the connection of G to the space V on which $\mathcal{H}$ operates. We shall find this mental degree of freedom very useful in the establishment of double groups as matrix groups below. (Furthermore, we shall find it useful to operate with representations $\mathcal{T}$ which are not always faithful).

We do not wish to imply by the above remarks that the operator representation viewpoint is the only advantageous way of looking at the connection between groups and the various linear spaces where we want them to "act". On the contrary, sometimes it may be desirable to regard the group elements as so intimately connected with the space that the mathematical concept of a module (over the group algebra) may be relevant. We shall not pursue this further here, but just mention a monography treating group representation theory from the module point of view [25].

## 3. Electronic Hamiltonians with a spin-orbit coupling term.

Let us consider a general N-electron molecular electronic Hamiltonian of the form

$$\mathcal{H} = \sum_{i=1}^{N} f(i) + \sum_{i<j}^{N} g(i,j) + \mathcal{H}_{SO}. \tag{3.1}$$

The first two terms make up the spin-free part of $\mathcal{H}$; explicitly, we have for the one-electron operator

$$f = -\tfrac{1}{2}\nabla^2 + v, \tag{3.2}$$

where $\nabla^2$ is the Laplacian and $v$ the potential created by the nuclei, while the two-electron operator is defined by

$$g(i,j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{for } 1 \leq i < j \leq N \tag{3.3}$$

(all in atomic units). The last term in (3.1) is the spin-orbit coupling operator, the explicit form of which is of importance for our analysis. We shall restrict attention to the case where it is a satisfactory approximation to take the spin-orbit coupling to be of the form

$$\mathcal{H}_{SO} = \sum_{i=1}^{N} \zeta\, \mathbf{l}_i \cdot \mathbf{s}_i, \tag{3.4}$$

where $\mathbf{l}_i$ is the orbital angular momentum of the i'th electron, $\mathbf{s}_i$ its spin angular momentum and $\zeta$ a suitable constant.

The assumption (3.4) requires a comment. The spin-orbit coupling term in a general molecular Hamiltonian results from a relativistic treatment of the electron and generally has a more complicated form [e.g., 26, Sec.3-3; 27, Chap.9; 28, Chap.2; 29-32]. The particular form (3.4) is a good approximation when the electrons move in a central potential. It is generally used in ligand field theory [6,32,33; see also Chapter 6 below]; this has been discussed in [31,32].

We shall have further comments to make on the form of the spin-orbit coupling operator below, after having introduced the double groups; until then, we ask the reader to accept (3.4) simply as a definition of the model operator we are going to study.

In order to be able to perform a group representation analysis of $\mathcal{H}$ in the sense of Chapter 2, we now intend to explain a little closer what is meant by (3.1)-(3.4). This will take up the rest of the present chapter, and readers who wish to do so may skip it, at least in a first reading.

The first point of interest is the structure of the Hilbert space on which $\mathcal{H}$ acts.

The orbital part of the description of electrons in molecules is usually - explicitly or implicitly - based on the Hilbert space $L^2(\mathbb{R}^3)$ consisting of the (equivalence classes of) square-integrable complex functions on three-dimensional space $\mathbb{R}^3$. Generally, orbitals - one-electron functions - are taken from some more or less explicitly specified closed subspace $V_0 \subseteq L^2(\mathbb{R}^3)$; for actual computation, $V_0$ is usually finite-dimensional, being spanned by the basis set of orbitals employed in the calculations. Spin is taken into account by giving each electron an extra degree of freedom with two possible expectation values, "spin up" (or "α spin") and "spin down" (or "β spin"). Mathematically, this may be effected in the one-electron description by forming the space $V_0 \otimes \mathbb{C}^2$, where $\mathbb{C}$ denotes the field of complex numbers. Here $\mathbb{C}^2$ is spanned by $\{\begin{pmatrix}1\\0\end{pmatrix}, \begin{pmatrix}0\\1\end{pmatrix}\}$, which is an orthonormal basis if the usual scalar product on $\mathbb{C}^2$ is used, and where we identify $\begin{pmatrix}1\\0\end{pmatrix}$ with α spin and $\begin{pmatrix}0\\1\end{pmatrix}$ with β spin.

In all, we shall consider the N-electron operator (3.1) as an operator on the Hilbert space $V = (V_0 \otimes \mathbb{C}^2)^{\otimes N}$.

In fact, because of the Pauli principle, all the physics of the N-electron system takes place in the totally anti-symmetric subspace of this N-fold tensor product space. However, this further qualification has no influence on the subsequent developments regarding double groups and will therefore be suppressed.

The sums of operators appearing in (3.1) are then to be interpreted in the appropriate way, e.g., the spin-orbit coupling term is understood to mean

$$\begin{aligned} & [\zeta\ \mathbf{l}\cdot\mathbf{s}] \otimes I \otimes \ldots\ldots \otimes I \\ + & I \otimes [\zeta\ \mathbf{l}\cdot\mathbf{s}] \otimes \ldots\ldots \otimes I \\ + & \ldots\ldots \\ + & I \otimes I \otimes \ldots\ldots \otimes [\zeta\ \mathbf{l}\cdot\mathbf{s}] \end{aligned} \tag{3.5}$$

where I is the identity operator on $V_o \otimes \mathbb{C}^2$. In the following it will be convenient for us to write

$$\mathcal{H} = \mathcal{H}_o + \mathcal{V} + \sum_{i=1}^{N} \zeta\ \mathbf{l}_i \cdot \mathbf{s}_i \tag{3.6}$$

with

$$\mathcal{H}_o = \sum_{i=1}^{N} (-\tfrac{1}{2}\nabla^2(i)) + \sum_{i<j}^{N} \mathcal{g}(i,j) \tag{3.7}$$

and

$$\mathcal{V} = \sum_{i=1}^{N} \boldsymbol{v}(i) \quad . \tag{3.8}$$

We shall focus our attention mostly on the last term, (3.4); to specify fully this operator, we need some more definitions.

The operators $\ell_x$, $\ell_y$, and $\ell_z$ on $V_o$ for the Cartesian components of orbital angular momentum (still in atomic units) are defined by

$$\ell_x = i\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right);$$

$$\ell_y = i\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right); \qquad (3.9)$$

and

$$\ell_z = i\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right).$$

Technical note: the operators $\ell_x$, $\ell_y$, and $\ell_z$ are only densely defined in $L^2(\mathbb{R}^3)$, but we shall assume that $V_o$ falls within their domains and that $V_o$ is invariant under all three of them. This requirement is usually fulfilled in practical calculations including spin-orbit coupling (to the extent that $V_o$ is at all specified beyond symmetry of the orbitals).

The operators $s_x$, $s_y$, and $s_z$ on $\mathbb{C}^2$ for the three Cartesian components of spin angular momentum may be defined by giving their matrices with respect to the above-mentioned basis for $\mathbb{C}^2$; they are $\frac{1}{2}\sigma_x$, $\frac{1}{2}\sigma_y$, and $\frac{1}{2}\sigma_z$, respectively, where the Pauli spin matrices are

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \qquad (3.10)$$

The operator $\mathbf{l}\cdot\mathbf{s}$ on $V_o \otimes \mathbb{C}^2$, appearing in the expression (3.5), is then defined by

$$\mathbf{l}\cdot\mathbf{s} = \ell_x \otimes s_x + \ell_y \otimes s_y + \ell_z \otimes s_z . \qquad (3.11)$$

It is thus the scalar product, in a tensor product sense, of the two operator-component vectors $\mathbf{l}$ and $\mathbf{s}$.

We have now discussed the operator defined by (3.1)-(3.4) in sufficient detail to be able to show in Chapter 4 how double groups naturally offer themselves as symmetry groups for this kind of operator.

## 4. Group representation analysis of the spin-orbit coupling - containing Hamiltonian: definition of double groups.

In order to perform a "group representation analysis" (Chapter 2) of the operator $\mathcal{H}$ in (3.6), one may start by considering the term $\mathcal{H}_0$. A frequent statement is that this term has "full spherical symmetry". Let us analyse what is meant by this.

Let O(3), also often denoted $R_{3i}$ or $K_h$, be the full rotation group in 3 dimensions, realized as the group of 3×3 real orthogonal matrices in the way discussed in Chapter 2. There is a well-known unitary*) representation $\mathcal{P}$ of O(3) on $L^2(R^3)$ (cf. Chapter 3), and thus on $V_0$ if it is invariant under $\mathcal{P}$, namely the one defined by

$$[\mathcal{P}(\mathbf{R})\psi](\mathbf{r}) = \psi(\mathbf{R}^{-1}\mathbf{r}) \qquad \text{for all } \mathbf{R} \in O(3) \qquad (4.1)$$

for all functions $\psi$ in the space considered. This is just the ordinary definition of the operation of "rotation of functions" (cf., e.g., [22, Chap.XIII, §11]); we already discussed this representation in Chapter 2.

What we mean by saying that $\mathcal{H}_0$ is spherically symmetrical is essentially that $\mathcal{H}_0$ commutes with all the operators $\mathcal{P}(\mathbf{R})$. However, $\mathcal{H}_0$ acts on the space $(V_0 \otimes C^2)^{\otimes N}$, so to make the statement precise, we must somehow make the operators $\mathcal{P}(\mathbf{R})$ act there, too. The simplest way to do this is to take the operators $[\mathcal{P}(\mathbf{R}) \otimes \mathcal{J}]^{\otimes N}$, where $\mathcal{J}$ denotes the identity operator on $C^2$. If we put G = O(3) and define

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*) The unitarity of $\mathcal{P}$ amounts to the fact that $\forall \psi, \varphi \in L^2(R^3)$ :
$<\mathcal{P}(\mathbf{R})\psi|\mathcal{P}(\mathbf{R})\varphi> = \int_{\mathbb{R}^3} \overline{\psi(\mathbf{R}^{-1}\mathbf{r})}\varphi(\mathbf{R}^{-1}\mathbf{r})d\mathbf{r} = \int_{\mathbb{R}^3} \overline{\psi(\mathbf{r})}\varphi(\mathbf{r})d\mathbf{r}$

$= <\psi|\varphi>$ for all $\mathbf{R} \in O(3)$, which is a well-known property of the integral.

$$\mathcal{T}(\mathbf{R}) = [\mathcal{P}(\mathbf{R}) \otimes \mathcal{I}]^{\otimes N} \quad \text{for } \mathbf{R} \in G \tag{4.2}$$

then we have a set-up completely analogous to the one described in Chapter 2. The statement that $\mathcal{H}_0$ is spherically symmetrical is equivalent to saying that this pair $(G, \mathcal{T})$ is a <u>symmetry group</u> for $\mathcal{H}_0$ (cf. [4, pp.90-92]).

In fact, for the operator on the right side of (4.2) to commute with $\mathcal{H}_0$, it would suffice to write just any operator on $\mathbb{C}^2$ as the second tensor factor. This is because $\mathcal{H}_0$ acts trivially on $\mathbb{C}^2$. We shall make use of this remark later in this chapter.

If we add on now the term $\mathcal{V}$ of (3.8), the pair $(O(3), \mathcal{T})$ is in general no longer a symmetry group. "The symmetry has been lowered" to some <u>subgroup</u> $G \subseteq O(3)$, a point group, meaning that while $(O(3), \mathcal{T})$ is not a symmetry group for $\mathcal{H}_0 + \mathcal{V}$, the pair $(G, \mathcal{T}_G)$ <u>is</u> a symmetry group for this new operator. Here we denote by $\mathcal{T}_G$ the restriction of the representation $\mathcal{T}$ from $O(3)$ to $G$. It is still immaterial whether we write $\mathcal{I}$ or any other operator as the second tensor factor in (4.2).

Now comes the interesting point: we include also the spin-orbit coupling term. To be able to investigate the consequences of this we need the following (well-known) property of the operators $\ell_x$, $\ell_y$, and $\ell_z$:

**<u>Proposition</u>** <u>1</u>. The operator set $\mathbf{l} = (\ell_x, \ell_y, \ell_z)$ "transforms under rotations as a pseudovector". In terms of the representation defined above, this means that

$$\mathcal{P}(\mathbf{R})(\ell_x \ \ell_y \ \ell_z)\mathcal{P}(\mathbf{R})^{-1} = (\ell_x \ \ell_y \ \ell_z)\ [(\det\mathbf{R})\mathbf{R}]$$
$$\text{for all matrices } \mathbf{R} \in O(3). \tag{4.3}$$

This is a compressed way of writing 3 equations; thus, taking out the x component of (4.3), we get

$$\mathcal{P}(\mathbf{R})\, \ell_x \mathcal{P}(\mathbf{R})^{-1} = (\det\mathbf{R}) \sum_{\nu = x,y,z} \mathbf{R}_{\nu x}\, \ell_\nu \tag{4.4}$$

Differently stated, the operator set **l** transforms under $\mathcal{P}$ as the particular real matrix form $\mathbf{D}_1$, defined by $\mathbf{D}_1(\mathbf{R}) = (\det\mathbf{R})\mathbf{R}$, of the irreducible representation $p_g$ of O(3).

> The result in Proposition 1 is 'physically' rather obvious from the definition of angular momentum. It may alas be verified by direct calculation. Thus, for example, (4.4) may be proved by showing that for any function $\psi$ and any matrix $\mathbf{R} = (\mathbf{R}_{ij})$, i,j = x,y,z, in O(3) we have
>
> $$[(\mathcal{P}(\mathbf{R})\ell_x \mathcal{P}(\mathbf{R})^{-1})\psi](\mathbf{r}) = [\det\mathbf{R}(\mathbf{R}_{xx}\ell_x + \mathbf{R}_{yx}\ell_y + \mathbf{R}_{zx}\ell_z)\psi](\mathbf{r}) \quad \text{for all } \mathbf{r} \in \mathbb{R}^3.$$
>
> For this, one uses the chain rule for partial differentiation when applying $\ell_x$, $\ell_y$, and $\ell_z$ according to definitions (3.9). Readers interested in the details may consult Appendix A.
>
> The transformation property of **l** thus established is put into a 'tensorial set' context in [24a, Eq.(47)] and in [24b, Sec.I.6].

Proposition 1 shows that after addition of the spin-orbit term the pair $(G,\mathcal{T}_G)$ with $\mathcal{T}$ defined in (4.2) will not in general be a symmetry group for the operator. Operating on $\mathbf{l}\cdot\mathbf{s}$ with $\mathcal{P}(\mathbf{R})\otimes\mathcal{J}$ for some $\mathbf{R}\in G$ will generally produce a mixture of all terms of the form $\ell_\alpha \otimes s_\beta$. (The reader may care to work out, as an exercise, what the symmetry of $\mathcal{H}_{SO}$ is under the representation $\mathcal{T}$ defined in (4.2).)

However, we shall see that invoking just one more substantial mathematical result we can find a natural symmetry group for the operator (3.6). Before we state this mathematical result as

Proposition 2, we recall two definitions: SU(2) is the group of unitary 2×2 matrices with determinant +1, and SO(3) is the subgroup of O(3), defined above, consisting of O(3)-matrices with determinant +1. Also, let **1** denote the 2×2 unit matrix and E the 3×3 unit matrix.

Alternative notations include $\mathbf{d}_3$, $R_3$, K, $O^+(3)$ and, unfortunately, even $O_3$ (in [5]) for SO(3); and $\mathbf{u}_2$ ($U_2$ in [5]), $R_3^*$, and K' for SU(2).

__Proposition__ _2_. There is a (in fact, precisely one) surjective ("onto") homomorphism $\pi$ : SU(2) → SO(3) such that

$$\mathbf{g}(\sigma_x\sigma_y\sigma_z)\mathbf{g}^{-1} = (\sigma_x\sigma_y\sigma_z)\pi(\mathbf{g}) \quad \text{for all } \mathbf{g} \in SU(2), \qquad (4.5)$$

where the Pauli spin matrices are defined in (3.10). The kernel $\{\mathbf{g} \in SU(2) \mid \pi(\mathbf{g}) = E\}$ of $\pi$ is the group $\{\mathbf{1}, -\mathbf{1}\}$ so that $\pi(\mathbf{g}) = \pi(-\mathbf{g})$ for all $\mathbf{g} \in SU(2)$.

Discussions of the relationship between SU(2) and SO(3) apparent from Proposition 2 are abundant ([4 , Sec.5.1]; [5]; [6 , §§6.9, 6.10]; [13, §II.11]; and references given below), but to get directly to the particular information stated in (4.5), see [7 , Sec.7.1]; [14, Chap.15]; [15, Sec.29]; or [16, §II.7]. Note that the last two references treat $\pi$ as the __adjoint__ __representation__ of SU(2) on its Lie algebra su(2) which is spanned by the Pauli matrices __all__ __multiplied__ __by__ $i$ (there is a misprint in [16]; $X_3$ at the bottom of p.78 should be multiplied by an $i$).

For the present we shall be satisfied with the information given in Proposition 2; in Sec.5.3 we shall describe more explicitly the homomorphism $\pi$.

Lest the reader feel that invoking Proposition 2 is "pulling the rabbit out of the hat", we stress that SU(2) or $R_3^*$ is the basis for angular momentum theory [__e.g.__, 6,7,9,14,22], although the group itself and its representations are not always used very explicitly;

and (4.5) may be viewed as stating a transformation property of the Pauli matrices quite analogous to (4.3) for the orbital angular momentum operators. So it is not unnatural to try and make use of this information in the present context.

In order to see what kind of application we can make of Proposition 2, we now start by noting that

$$\mathcal{P}(\pi(\mathbf{g}))\,(\ell_x\ \ell_y\ \ell_z)\,\mathcal{P}(\pi(\mathbf{g}))^{-1} = (\ell_x\ \ell_y\ \ell_z)\mathbf{D}_1(\pi(\mathbf{g})) \quad \text{for all } \mathbf{g} \in SU(2); \qquad (4.6)$$

this follows from (4.3) just by replacing $\mathbf{R}$ by $\pi(\mathbf{g})$. Furthermore, we may rewrite (4.5) as

$$\Pi(\mathbf{g})\,(s_x\, s_y\, s_z)\,\Pi(\mathbf{g})^{-1} = (s_x\, s_y\, s_z)\mathbf{D}_1(\pi(\mathbf{g})) \quad \text{for all } \mathbf{g} \in SU(2) \qquad (4.7)$$

if we define $\Pi(\mathbf{g})$ to be the operator on $\mathbb{C}^2$ having the matrix $\mathbf{g}$ with respect to the orthonormal basis for $\mathbb{C}^2$ mentioned in Chapter 3. (Thus, (4.7) is just the operator equation corresponding to the matrix equation (4.5).) Comparing (4.6) and (4.7), we see that we have two very similar situations: the operator set $\mathbf{l}$ transforms under the representation $\mathcal{P}\circ\pi$ as the real matrix representation $\mathbf{D}_1 \circ \pi$ of SU(2), and the set $\mathbf{s}$ transforms under $\Pi$ as the <u>same</u> real matrix representation of SU(2). From this it may actually be easily shown that $\mathbf{l}\cdot\mathbf{s} = \ell_x \otimes s_x + \ell_y \otimes s_y + \ell_z \otimes s_z$ commutes with all the operators $(\mathcal{P}\circ\pi(\mathbf{g}))\otimes\Pi(\mathbf{g})$, $\mathbf{g} \in SU(2)$, on $V_o \otimes \mathbb{C}^2$ and thus that $(SU(2), [(\mathcal{P}\circ\pi)\otimes\Pi]^{\otimes N})$ <u>is a symmetry group for the spin-orbit coupling term</u> (3.5). The necessary arguments are given in Appendix B.

At this point we owe the reader a comment. By the symbol "$\circ$" we generally mean composition of mappings, i.e., $D_1 \circ \pi$ is the mapping defined by

$$D_1 \circ \pi(g) = D_1(\pi(g)). \qquad (4.8)$$

Thus, $D_1 \circ \pi$ is indeed a real matrix representation of SU(2) (since $D_1$ is a real matrix representation of SO(3)). Furthermore, $\mathcal{P} \circ \pi$ is an operator representation of SU(2) on the space $V_o$. The tensor-power-of-tensor-product mapping $[(\mathcal{P} \circ \pi) \otimes \Pi]^{\otimes N}$ is the operator representation of SU(2) on $(V_o \otimes \mathbb{C}^2)^{\otimes N}$ defined by

$$[(\mathcal{P} \circ \pi) \otimes \Pi]^{\otimes N}(g) = [\mathcal{P}(\pi(g)) \otimes \Pi(g)]^{\otimes N}$$
$$\text{for all } g \in SU(2). \qquad (4.9)$$

Returning to the full Hamiltonian (3.6), we recall that $\mathcal{H}_o + \mathcal{V}$ had a symmetry group $(G, \mathcal{T})$ with $G \subseteq O(3)$ and $\mathcal{T}$ defined in (4.2). Our goal is now to construct a symmetry group for $\mathcal{H}$ which as far as possible "contains" this G-symmetry <u>as well as</u> the SU(2)-symmetry of the term (3.5) just established.

Contemplating this requirement rather naturally leads one to looking for triples $(G^*, \eta, \xi)$, where $G^*$ is a group and $\eta : G^* \to O(3)$ and $\xi : G^* \to SU(2)$ are homomorphisms such that

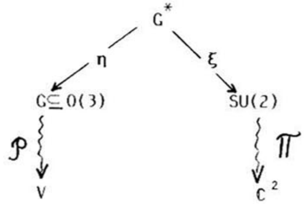
(i) $\eta(G^*) = G$;

(ii) $D_1(\eta(g)) = D_1(\pi(\xi(g)))$

for all $g \in G^*$, i.e., $D_1 \circ \eta = D_1 \circ \pi \circ \xi$.

<u>For such a triple</u>, $(G^*, [(\mathcal{P} \circ \eta) \otimes (\Pi \circ \xi)]^{\otimes N})$ <u>will be a symmetry group for</u> $\mathcal{H}$.

The idea behind (i) and (ii) may be illustrated by the following diagram:




(4.10)

The mappings $\eta$ and $\xi$ are going to help us represent just one group, namely $G^*$, in orbital space as well as spin space. We know that if $g \in G^*$ with $\eta(g) \in G$, then $\mathcal{P}(\eta(g)) \otimes \mathcal{O}$ will commute with $\mathcal{H}_0 + \mathcal{V}$ irrespective of what the operator $\mathcal{O}$ is (see remarks following (4.2)) and $\mathcal{P}(\eta(g))$ will transform the set $(\ell_x\ \ell_y\ \ell_z)$ by the matrix $\mathbf{D}_1(\eta(g))$ (see (4.3)). We also know that $\Pi(\xi(g))$ will transform the set $(s_x\ s_y\ s_z)$ by the matrix $\mathbf{D}_1(\pi(\xi(g))$ (see (4.7)). So if (ii) is satisfied, we are again in the situation that we have an operator representation $(\mathcal{P} \circ \eta)$ of our group on the orbital space which transforms $\mathbf{l}$ according to a certain real matrix representation $(\mathbf{D}_1 \circ \eta)$ and an operator representation on the spin space $(\Pi \circ \xi)$ which transforms $\mathbf{s}$ according to the same real matrix representation of the group; thus the arguments of Appendix B are again applicable, and the above assertion about the operator representation $[(\mathcal{P} \circ \eta) \otimes (\Pi \circ \xi)]^{\otimes N}$ of $G^*$ on $(V_0 \otimes \mathbb{C}^2)^{\otimes N}$ follows. Requirement (i) just ensures that we do not loose any of the G-symmetry (including possible improper rotations) in constructing $G^*$ and connecting it to the orbital part of the problem by the use of $\eta$.

We shall now demonstrate that one may, in fact, construct such a triple $(G^*, \eta, \xi)$ for any group $G \subseteq O(3)$. We shall distinguish three cases and in each case define the group $G^*$ and the homomorphisms $\eta$ and $\xi$ explicitly. Every time we shall then prove that conditions (i) and (ii) are satisfied. Readers who are only interested in the structure of $G^*$ may skip the discussion of the three cases and go directly to the subsequent summary.

<u>**Case**</u> <u>1</u>. Suppose $G \subseteq SO(3)$, <u>i</u>.<u>e</u>., G consists only of proper rotations. Here there is an obvious solution: We put $G^* = \pi^{-1}(G)$, whereby we mean that $G^* = \{\mathbf{g} \in SU(2) \mid \pi(\mathbf{g}) \in G\}$; we define $\eta$ by $\eta(\mathbf{g}) = \pi(\mathbf{g})$ for $\mathbf{g} \in G^*$; and we define $\xi$ by $\xi(\mathbf{g}) = \mathbf{g}$ for $\mathbf{g} \in G^*$.

[To see that the triple $(G^*,\eta,\xi)$ hereby satisfies (i) and (ii), observe that $\eta(G^*) = \pi(G^*) = \pi(\pi^{-1}(G)) = G$ (because $\pi$ is surjective) and that $\mathbf{D}_1(\eta(\mathbf{g})) = \mathbf{D}_1(\pi(\mathbf{g})) = \mathbf{D}_1(\pi(\xi(\mathbf{g})))$ for all $\mathbf{g} \in G^*$ (because $\xi(\mathbf{g}) = \mathbf{g}$).]

<u>**Case**</u> <u>2</u>. Suppose next that $G \subseteq O(3)$ with $-E \in G$, that is, G contains the inversion $-\mathbf{E}$. Put $G_o = G \cap SO(3)$, the intersection of G with SO(3) or, alternatively, the subgroup of G consisting of only the proper rotations. Then G is the direct product of G and the subgroup $\{E,-E\}$ of order 2.

Since $\mathbf{D}_1$ has the property that $\mathbf{D}_1(\mathbf{RS}) = \mathbf{D}_1(\mathbf{R})\mathbf{D}_1(\mathbf{S}) = \mathbf{D}_1(\mathbf{R})$ for $\mathbf{R} \in G_o$ and $\mathbf{S} \in \{E,-E\}$, it is rather natural to put here $G^* = G_o^* \times \{E,-E\}$, to put $\eta(\mathbf{g},\mathbf{S}) = \pi(\mathbf{g})\mathbf{S}$ for $\mathbf{g} \in G_o^*$ and $\mathbf{S} \in \{E,-E\}$, and to put $\xi(\mathbf{g},\mathbf{S}) = \mathbf{g}$ for $(\mathbf{g},\mathbf{S}) \in G^*$.

[Note that $G_o^*$ is defined because $G_o$ belongs to case 1. For a demonstration of the assertion regarding the direct product structure of G, see Appendix C.

It is readily verified that $\eta$, defined in this way, is a homomorphism with property (i). And if $(\mathbf{g},\mathbf{S}) \in G^*$, we have $\mathbf{D}_1(\eta(\mathbf{g},\mathbf{S})) = \mathbf{D}_1(\pi(\mathbf{g})\mathbf{S}) = \mathbf{D}_1(\pi(\mathbf{g})) = \mathbf{D}_1(\pi(\xi(\mathbf{g},\mathbf{S})))$, so that (ii) is also satisfied.]

<u>**Case**</u> <u>3</u>. The final case is that of G being a subgroup of O(3) with $G \subseteq SO(3)$ and $-E \notin G$, <u>i</u>.<u>e</u>., G contains improper rotations, but not the inversion. We consider the set $G' = \{(\det \mathbf{R})\mathbf{R} \mid \mathbf{R} \in G\}$ which is a subgroup of SO(3) isomorphic to G; an isomorphism is $\psi: G \to G'$ defined by $\psi(\mathbf{R}) = \mathbf{D}_1(\mathbf{R}) = (\det \mathbf{R})\mathbf{R}$.

We then put $G^* = (G')^*$; define $\eta$ by $\eta(\mathbf{g}) = \psi^{-1}(\pi(\mathbf{g}))$ for all $\mathbf{g} \in G^*$; and define $\xi$ by $\xi(\mathbf{g}) = \mathbf{g}$ for $\mathbf{g} \in G^*$.

[ Regarding the isomorphism of G and G', see Appendix C. Clearly, $\eta$ will be a homomorphism with

$$\eta(G^*) = \psi^{-1}(\pi(\pi^{-1}(G'))) = \psi^{-1}(G') = G,$$

using that $\pi$ is surjective. To check (ii), observe that

$$\mathbf{D}(\eta(\mathbf{g})) = \mathbf{D}(\psi^{-1}(\pi(\mathbf{g}))) = \mathbf{D}(\pi(\mathbf{g})) = \mathbf{D}(\pi(\xi(\mathbf{g})))$$

for all $\mathbf{g} \in G^*$, because $\mathbf{D}(\psi(\mathbf{R})) = \mathbf{D}(\mathbf{R})$ for all $\mathbf{R} \in G$ and thus $\mathbf{D}(\psi^{-1}(\mathbf{R})) = \mathbf{D}(\mathbf{R})$ for all $\mathbf{R} \in G'$. ]

In practice, one will usually not need to operate explicitly with the homomorphisms $\eta$ and $\xi$. Let us therefore summarize just the definitions of $G^*$ itself suggested in the three cases:

(1) If G is a proper point group, $G^*$ is defined to be $\pi^{-1}(G)$, where $\pi$ is the homomorphism from SU(2) onto SO(3) introduced in Proposition 2.

(2) If G is a point group containing the inversion and with proper rotation subgroup $G_0$, i.e., if $-\mathbf{E} \in G$ and $G_0 = \{\mathbf{R} \in G \,|\, \det\mathbf{R} = +1\}$, then $G^*$ is defined to be the (outer) direct product $G_0^* \times S_2$, where $G_0^*$ is defined in (1).

(3) If G is an improper point group which does not contain the inversion, $G^*$ is defined to be $(G')^*$, where G' is the proper point group $\{(\det\mathbf{R})\mathbf{R} \,|\, \mathbf{R} \in G\}$ isomorphic to G.

For each group $G \subseteq O(3)$, the group $G^*$ thus defined will be called the double group of G (or the spinor group of G, cf. [6, §§6.9 and 6.11]). This terminology will be justified in Chapter 5. Definition (1) is that of Opechowski [2], and all three definitions coincide with those of, for example, [4, Sec.5.1];

[6, §§6.9 and 6.11]; and [8, Sec.16]. In cases (1) and (3), the double groups are groups of $2 \times 2$ matrices.

Table 1 lists the resulting double groups for the improper point groups.

Note that within the present framework the definition of double groups of improper point groups derives in a natural way from the pseudo-vector character of the orbital angular momentum. Thus we do not have to introduce the device of an even (gerade) "intrinsic" parity of spin functions (cf. [6, §6.9]; [8, Sec.11]; [9, p.140]), a concept which is rather confusing because the spatial rotations (i.e., the O(3)-elements) - especially the improper ones - are not in an obvious way representable on the spin space $C^2$. We point out that isomorphic point groups may according to the definitions suggested have non-isomorphic double groups; this is not unreasonable since isomorphic point groups may well have different physical significance, i.e., a different relation to the orbital angular momentum operators (Table 1 gives examples of this situation).

Remarks.

$1^{\circ}$ The reader may be wondering whether one could obtain an even more satisfactory treatment of the improper point groups if one could replace the homomorphism $\pi$ of Proposition 2 by some homomorphism covering the whole of O(3). One might, for example, ask if there is a homomorphism from U(2) onto O(3), i.e., whether it would help to relax the condition that the $2 \times 2$ unitary matrices have determinant +1 as in SU(2). Extending $\Pi$ defined above in the natural way to U(2) gives still only SO(3) as the image, i.e., one cannot "hit" the improper rotations; and it actually turns out that the question asked can generally be answered negatively: Suppose $\pi'$ was such a homomorphism of U(2) onto O(3). There is a homomorphism of O(3) onto the group $\{1, -1\}$, namely, the irreducible representation $s_u$ defined by

$$s_u(\mathbf{R}) = \det\mathbf{R} \quad \text{for } \mathbf{R} \in O(3) .$$

Some element $\mathbf{g}$ of U(2) would by the composed homomorphism $\psi = s_u \circ \pi'$ be mapped onto -1. However, it is easily shown (exercise!) that any matrix $\mathbf{g}$ in U(2) has a square root in U(2), i.e., a matrix $\mathbf{h}$ such that $\mathbf{h}^2 = \mathbf{g}$. We would then have

$$-1 = \psi(\mathbf{g}) = \psi(\mathbf{h}^2) = \psi(\mathbf{h})^2$$

which is impossible since $\psi(h)$ is either 1 or -1.

On the other hand, we are not implying that one could not develop a different theory which did not involve $2 \times 2$ matrices at all (or involved them in some other way than done here). This is a separate problem; our goal here was specifically to explain how the above-defined double groups naturally arise in the context described.

$2^0$ The construction of the double groups discussed as cases 1-3 above may be described in a maybe more unified way by starting with the particular case G = O(3). We get the situation

$$\begin{array}{ccc} & O(3)^* = SU(2) \times S_2 & \\ \eta \swarrow & & \searrow \xi \\ O(3) & & SU(2) \end{array} \qquad (4.11)$$

with $\eta$ and $\xi$ defined as in case 2, and using that $SO(3)^* = SU(2)$ by case 1. Then for any group $G \subseteq O(3)$ we define $G^* = \eta^{-1}(G)$ and use as $\eta$ and $\xi$ for $G^*$ the restrictions to $G^*$ of $\eta$ and $\xi$ in (4.11). The reader may think over that in this way we may represent the most general situation by the following diagram:

$$\begin{array}{ccc} & G^* \subseteq SU(2)\times S_2 & \\ \swarrow \eta & & \searrow \xi \\ G \subseteq O(3) & & (G \cap SO(3))^* \subseteq SU(2) \end{array} \qquad (4.12)$$

with $(G \cap SO(3))^* = \pi^{-1}(G \cap SO(3))$.

$3^o$ We mentioned in Section 3 that (3.4) is not the most general form of the spin-orbit coupling operator. In the present context, the question which arises is whether the double groups as defined here are still symmetry groups if we use one of the more general forms of the spin-orbit coupling operator. If the operator set $\mathbf{l}$ is replaced by an operator set $(\sigma_x, \sigma_y, \sigma_z)$ proportional to $\nabla \mathcal{V} \times \mathbf{p}$ [e.g., 26, Sec.3-3; 27, Chap.9; 29], it seems plausible that the transformation property

$$\mathcal{P}(\eta(g))\,(\sigma_x\,\sigma_y\,\sigma_z)\,\mathcal{P}(\eta(g))^{-1} = (\sigma_x\,\sigma_y\,\sigma_z)\,\mathbf{D}_1(\eta(g)) \quad \text{for all } g \in G^* \qquad (4.13)$$

(cf. discussion following (4.10)) will be preserved, considering that the potential $\mathcal{V}$ has G-symmetry; but we have not worked out a formal proof of this like the one given in Appendix A for $\mathbf{l}$. For the approximate form discussed by Misetich and Buch for application in ligand-field theory [32; see also 34, Sec.10.45],a similar remark could be made. In purely symmetry-based ligand-field theory, one simply assumes the spin-orbit coupling operator to have the same symmetry as (3.4) (see [33, Chap.6] and Chapter 6 below) so that the above-defined double groups by definition are symmetry groups for the Hamiltonian.

## 5. General properties of double groups.

We shall restrict considerations in this section to subgroups of SO(3) and their double groups. In this way we cover cases (1) and (3) [see end of Chapter 4]; information on double groups falling in class (2) is obtained by using the direct product structure $G_o^* \times S_2$ and the separate properties of $G_o^*$ and $S_2$.

### 5.1. Introductory remarks.

Once one has accepted the definition of double groups of proper point groups given above, Opechowski's exposition ([2]; see also [4, Sec.5.1]) can be consulted for information on these groups. In particular, one finds there theorems concerning the not entirely trivial question of the conjugacy class structure of the double groups. There is no need to go through these considerations here, but we do point out a few important general properties of double groups in Section 5.2.

For practical applications, however, one will often just need the character table of a given double group. Such character tables are readily available ([6, App.2; 10; 11; 12 ]; see also historical remarks in Chapter 7), although not always completely free of error. The tools needed for a more quantitative application of double groups, viz., explicit matrix representations and corresponding coupling (Clebsch-Gordan) coefficients and 3-Γ symbols, are also increasingly becoming available; see [23]. This whole apparatus may for many purposes be used without a detailed description of the individual double group elements, their mutual relations, their distributions on the conjugacy classes, and their relations with the elements of the "single group". However, for such more detailed discussions, a suitable parametrization of the point groups and their double groups may be desirable, and we therefore give this aspect some attention in Section 5.3.

## 5.2. General structural features of double groups.

Suppose G is a subgroup of SO(3) and $G^* = \pi^{-1}(G) \subseteq SU(2)$ is its double group. Then $G^*$ has the following property:

The group $\{\mathbf{1},-\mathbf{1}\}$ is a normal subgroup of $G^*$, and the quotient group $G^*/\{\mathbf{1},-\mathbf{1}\}$ is isomorphic to G. Thus if G is finite, $G^*$ is also finite and its order is twice that of G.

This property justifies the term "double group".

Note that we can not in general conclude from this that $G^*$ has a subgroup isomorphic to G. In this sense the formulation that $G^*$ is an "augmented group" (cf. Section 5.3) is unfortunate; however, it would be mathematically correct to say that $G^*$ is a central extension of $\{\mathbf{1},-\mathbf{1}\}$ by G [4, p.127; 35, Chap.7], because $\{\mathbf{1},-\mathbf{1}\}$ is contained in the center of $G^*$ and $G^*/\{\mathbf{1},-\mathbf{1}\} \simeq G$.

To have a specific example, we have listed the elements of the dihedral double group $D_2^*$ in Table 2. It is quite evident that $D_2^*$ does not have a subgroup isomorphic to $D_2$, because $D_2$ has 3 elements of order 2, whereas there is only one such element (namely, $-\mathbf{1}$) in $D_2^*$. [We have given in Table 2 also the character table of $D_2^*$ together with that of the dihedral group $D_4$, because these two groups are a nice example of non-isomorphic groups having the same character table.]

On the other hand, in Section 5.3 we shall see that the double group $C_n^*$ of the cyclic group $C_n$ is isomorphic to $C_{2n}$ for $n = 1,2,3$ ...; and since $C_{2n}$ has a subgroup isomorphic to $C_n$, we conclude that there are some cases where $G^*$ has a subgroup isomorphic to G.

All the above mathematical statements are easily proved from the definition of double groups. The reader may further convince himself that a subgroup of SU(2) is, in fact, the double group of some subgroup of SO(3) if and only if it contains **-1**. A finite subgroup of SU(2) is then a double group if and only if it has even order (to see "if", use that a group of even order has at least one element of order 2 and that the only element of order 2 in SU(2) is **-1**). For further information on particular double groups, see the references given in Chapter 7.

There is a very important remark to be made concerning different matrix forms of a given "abstract" point group. Relative to a fixed coordinate system, we are of course free to choose the defining axes of the symmetry operations in the point group and thus may obtain different (but of course isomorphic, actually even conjugate, cf. Appendix D) matrix versions in O(3) of the point group. These will in general give different concrete double groups, but luckily these are also isomorphic (and even conjugate). We prove this in Appendix D. Thus, looking again at Table 2, $D_2^*$ is not necessarily the particular subgroup of SU(2) given there, but it will always be a subgroup of SU(2) conjugate to that one.

## 5.3. Parametrizations of the double groups.

Any matrix $\mathbf{g} \in SU(2)$ may be written

$$\mathbf{g} = \begin{pmatrix} \alpha & -\bar{\beta} \\ \beta & \bar{\alpha} \end{pmatrix} \qquad (5.1)$$

where $\alpha$ and $\beta$ are complex numbers with $|\alpha|^2 + |\beta|^2 = 1$ (and any such matrix belongs to SU(2)).

We shall need an explicit description of the homomorphism $\pi$: SU(2) → SO(3) introduced in Proposition 2 (Chapter 4). If $\mathbf{g}$ is given by (6.1), then *)

$$\pi(\mathbf{g}) = \begin{pmatrix} \frac{1}{2}[\alpha^2 + \bar{\alpha}^2 - \beta^2 - \bar{\beta}^2] & -\frac{i}{2}[\alpha^2 - \bar{\alpha}^2 - \beta^2 + \bar{\beta}^2] & \alpha\bar{\beta} + \bar{\alpha}\beta \\ \frac{i}{2}[\alpha^2 - \bar{\alpha}^2 + \beta^2 - \bar{\beta}^2] & \frac{1}{2}[\alpha^2 + \bar{\alpha}^2 + \beta^2 + \bar{\beta}^2] & i[\alpha\bar{\beta} - \bar{\alpha}\beta] \\ -[\alpha\beta + \bar{\alpha}\bar{\beta}] & i[\alpha\beta - \bar{\alpha}\bar{\beta}] & |\alpha|^2 - |\beta|^2 \end{pmatrix}. \quad (5.2)$$

The derivation of formula (5.2) is straightforward; for example, to obtain the second column, calculate

$$\mathbf{g}\sigma_y\mathbf{g}^{-1} = \begin{pmatrix} \alpha & -\bar{\beta} \\ \beta & \bar{\alpha} \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \bar{\alpha} & \bar{\beta} \\ -\beta & \alpha \end{pmatrix} = \begin{pmatrix} i\alpha\beta - i\bar{\alpha}\bar{\beta} & -i\alpha^2 - i\bar{\beta}^2 \\ i\bar{\alpha}^2 + i\beta^2 & -i\alpha\beta + i\bar{\alpha}\bar{\beta} \end{pmatrix}$$

$$= -\frac{i}{2}[\alpha^2 - \bar{\alpha}^2 - \beta^2 + \bar{\beta}^2]\sigma_x + \frac{1}{2}[\alpha^2 + \bar{\alpha}^2 + \beta^2 + \bar{\beta}^2]\sigma_y + i[\alpha\beta - \bar{\alpha}\bar{\beta}]\sigma_z .$$

One could of course now parametrize SU(2) and its subgroups simply by the pairs $(\alpha,\beta)$ (which are equivalent to the Cayley-Klein parameters [37, Sec.4-5]). However, as is obvious from (5.2), these parameters are not useful for discussing the relation between $\mathbf{g}$ and $\pi(\mathbf{g})$. We therefore now prepare to introduce another parametrization of SU(2).

Since $|\alpha|^2 + |\beta|^2 = 1$, it is not unnatural to put $|\alpha| = \cos\omega$ and $|\beta| = \sin\omega$ with $0 \le \omega \le \frac{\pi}{2}$. Then $\alpha = |\alpha|e^{i\chi} = e^{i\chi}\cos\omega$ for some real $\chi$ with $0 \le \chi < 2\pi$ and $\beta = |\beta|e^{i\xi} =$

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*) When looking up formulae like (5.2) in the literature, e.g., the references given after Proposition 2 in Chapter 4, one should be aware that phase differences may arise for various reasons. For example, in [15, Sec.29], one uses $-\sigma_y$ instead of $\sigma_y$ and thus gets a sign change 4 places in the matrix in (5.2).

$e^{i\xi}\sin\omega$ for some real $\xi$ with $0 \leq \xi < 2\pi$. In this way **g** becomes the matrix

$$\begin{pmatrix} e^{i\chi}\cos\omega & -e^{-i\xi}\sin\omega \\ e^{i\xi}\sin\omega & e^{-i\chi}\cos\omega \end{pmatrix}$$

$$= \begin{pmatrix} e^{-i(\xi-\chi)/2} & 0 \\ 0 & e^{i(\xi-\chi)/2} \end{pmatrix} \begin{pmatrix} \cos\omega & -\sin\omega \\ \sin\xi & \cos\xi \end{pmatrix} \begin{pmatrix} e^{i(\xi+\chi)/2} & 0 \\ 0 & e^{-i(\xi+\chi)/2} \end{pmatrix}. \tag{5.3}$$

As will be clear immediately below, it is convenient to rename the parameters in (5.3) by putting $\theta = 2\omega$, $\varphi = \xi-\chi$, and $\psi = -(\xi+\chi)$; we then get

$$\mathbf{g}(\varphi,\theta,\psi) = \begin{pmatrix} e^{-i\varphi/2} & 0 \\ 0 & e^{i\varphi/2} \end{pmatrix} \begin{pmatrix} \cos\frac{1}{2}\theta & -\sin\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta & \cos\frac{1}{2}\theta \end{pmatrix} \begin{pmatrix} e^{-i\psi/2} & 0 \\ 0 & e^{i\psi/2} \end{pmatrix}$$

$$= \begin{pmatrix} e^{-i(\varphi+\psi)/2}\cos\frac{1}{2}\theta & -e^{-i(\varphi-\psi)/2}\sin\frac{1}{2}\theta \\ e^{i(\varphi-\psi)/2}\sin\frac{1}{2}\theta & e^{i(\varphi+\psi)/2}\cos\frac{1}{2}\theta \end{pmatrix}$$

$$\text{with } 0 \leq \theta \leq \pi; \quad 0 \leq \varphi < 2\pi; \quad 0 \leq \psi < 4\pi. \tag{5.4}$$

We have contracted the parameter interval for $\varphi$ from $-2\pi < \varphi < 2\pi$ to $0 \leq \varphi < 2\pi$ since for any $\varphi$ between 0 and $2\pi$ we have

$$\mathbf{g}(\varphi-2\pi,\theta,\psi) = -\mathbf{g}(\varphi,\theta,\psi) = \begin{cases} \mathbf{g}(\varphi,\theta,\psi+2\pi) & \text{for } 0 \leq \psi < 2\pi \\ \mathbf{g}(\varphi,\theta,\psi-2\pi) & \text{for } 2\pi \leq \psi < 4\pi \end{cases}. \tag{5.5}$$

Now since $\boldsymbol{\pi}$ is a homomorphism, we have

$$\boldsymbol{\pi}(\mathbf{g}(\varphi,\theta,\psi))$$

$$= \boldsymbol{\pi}\left(\begin{pmatrix} e^{-i\varphi/2} & 0 \\ 0 & e^{i\varphi/2} \end{pmatrix}\right) \boldsymbol{\pi}\left(\begin{pmatrix} \cos\frac{1}{2}\theta & -\sin\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta & \cos\frac{1}{2}\theta \end{pmatrix}\right) \boldsymbol{\pi}\left(\begin{pmatrix} e^{-i\psi/2} & 0 \\ 0 & e^{i\psi/2} \end{pmatrix}\right). \tag{5.6}$$

Using (5.2) gives

$$\pi\left(\begin{pmatrix} e^{-i\varphi/2} & 0 \\ 0 & e^{i\varphi/2} \end{pmatrix}\right) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} = \mathbf{R}(\varphi,0,0); \qquad (5.7a)$$

$$\pi\left(\begin{pmatrix} \cos\frac{1}{2}\theta & -\sin\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta & \cos\frac{1}{2}\theta \end{pmatrix}\right) = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} = \mathbf{R}(0,\theta,0); \qquad (5.7b)$$

$$\pi\left(\begin{pmatrix} e^{-i\psi/2} & 0 \\ 0 & e^{i\psi/2} \end{pmatrix}\right) = \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} = \mathbf{R}(0,0,\psi). \qquad (5.7c)$$

Evidently the matrices $\mathbf{R}(\varphi,0,0)$, $\mathbf{R}(0,\theta,0)$, and $\mathbf{R}(0,0,\psi)$ defined in Eqs.(5.7) are the matrices of, respectively, an anti-clockwise rotation around the Z axis through an angle $\varphi$, an anti-clockwise rotation around the Y axis through an angle $\theta$, and an anti-clockwise rotation around Z through an angle $\psi$. Thus $(\varphi,\theta,\psi)$ are <u>Euler angles</u>*) for the rotation with matrix $\pi(\mathbf{g}(\varphi,\theta,\psi))$.

Clearly the parameters $\varphi,\theta,\psi$ are well suited for describing the relationships between elements of a subgroup $G \subseteq SO(3)$ and elements of its double group $G^* \subseteq SU(2)$. Suppose one has an element $\mathbf{R} \in G$. Then $\mathbf{R}$ can be written - not necessarily uniquely as $\mathbf{R}(\varphi,\theta,\psi) = \mathbf{R}(\varphi,0,0)\mathbf{R}(0,\theta,0)\mathbf{R}(0,0,\psi)$ with $0 \leq \varphi < 2\pi$; $0 \leq \theta \leq \pi$; $0 \leq \psi < 2\pi$. Exactly two elements in $G^*$ correspond to $\mathbf{R}$, namely, $\mathbf{g}(\varphi,\theta,\psi)$ and $-\mathbf{g}(\varphi,\theta,\psi) = \mathbf{g}(\varphi,\theta,\psi+2\pi)$; that is, $\pi$ maps exactly these two elements of $G^*$ onto $\mathbf{R}$. One might then decide to designate $\mathbf{g}(\varphi,\theta,\psi)$ as $\mathbf{R}^*$ and $\mathbf{g}(\varphi,\theta,\psi+2\pi)$ as $-\mathbf{R}^*$.

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*) There are various definitions of Euler angles. For others than the present one, see [7, Sec.7.1; 22,pp.1068 ff.; 36, Chap.5 and App.D]; for comments on the literature and comparisons of conventions see [37, Sec.s 4-4 and 4-5; 38; 39]. For the connection with other parametrizations, see, <u>e.g.</u>, [40].

Such a convention has the advantage that one can name the elements of the double group using the symbols for the geometric rotations to which they correspond. It avoids the difficulties associated with the "classical" double group notation ([1]; or see tables like those in [6, App.2]), where one insists on representing half of the elements in the double group by symbols identical to those of the "single" group elements. Thus the problems pointed out by Altmann [18a] disappear; for example, for any element $\mathbf{R} \in G$, the relations

$$\mathbf{R}^*(\mathbf{R}^*)^{-1} = \mathbf{1} \tag{5.8a}$$

and

$$(-\mathbf{R}^*)(-\mathbf{R}^*)^{-1} = \mathbf{1} \tag{5.8b}$$

are - trivially - satisfied (although we do not necessarily have, say, $\mathbf{R}^*(\mathbf{R}^{-1})^* = \mathbf{1}$).

Of course the convention for notation suggested here depends on how one chooses Euler angles to describe the rotations (cf. legend to Table 2). However, this is no worse than the situation in the point groups themselves, where e.g., the designation of a rotation as $\mathbf{C}_3$, as opposed to $\mathbf{C}_3^{-1}$, or as $\mathbf{C}_2^X$, as opposed to $\mathbf{C}_2^Y$ or $\mathbf{C}_2^Z$, depends on having some sort of a convention regarding orientation of rotation axes and positive and negative sense of rotation angles. Thus the description of the conjugacy class structure of the double groups (one of the problematic aspects mentioned in [18a]) is no more difficult than that of the point groups. [Consider, with reference to the $\mathbf{C}_3$ and $\mathbf{C}_2$ examples above, the groups T and $D_2$; see the case of $D_2^*$ in Table 2].

In fact, the example given in connection with Table 2 represents the only situation with trouble arising from non-uniqueness of the angles $(\varphi,\theta,\psi)$. The angles $(\varphi,\theta,\psi)$ as used here, with the parameter intervals stated in (5.4), are unique except when $\theta = 0$ or $\theta = \pi$ ; this is easily seen from the matrix given in (5.4). For our notation convention, only $\theta = \pi$ gives problems; here, $\varphi$ and $\psi$ may be changed arbitrarily as long as $\varphi - \psi$ is unchanged modulo $4\pi$. A further convention might be, then, to take the minimum value of $\varphi$ for the Fuler angles of the given rotation before going on to $\mathbf{g}(\varphi,\theta,\psi)$.

A note is in its place here concerning the order of elements. Generally, $\mathbf{R}$ and $-\mathbf{R}^*$ may be of the same even order or one of these double group elements may be of an odd order n and the other one then of order 2n. Examples: if $\mathbf{C}_4 = \mathbf{R}(\pi/2,0,0)$, then $\mathbf{C}_4^* = \mathbf{g}(\pi/2,0,0)$ and $-\mathbf{C}_4^* = \mathbf{g}(\pi/2,0,2\pi)$, and both are of order 8; if $\mathbf{C}_3 = \mathbf{R}(2\pi/3,0,0)$, then $\mathbf{C}_3^* = \mathbf{g}(2\pi/3,0,0)$ and $-\mathbf{C}_3^*(2\pi/3,0,2\pi)$, the first of these being of order 6 and the other one of order 3. On the other hand, had $\mathbf{C}_3$ been $\mathbf{R}(4\pi/3,0,0)$, we would have had $\mathbf{C}_3^*$ to be of order 3 and $-\mathbf{C}_3^*$ to be of order 6.

We close this section by using the above formulas to examine the double groups $C_n^*$ for the cyclic groups $C_n$ ($n = 1,2,3...$ ; $\infty$). Suppose $\mathbf{R}_\varphi \in SO(3)$ denotes a rotation around the Z axis through an angle $\varphi$ with $0 \leq \varphi < 2\pi$, that is, $\mathbf{R}_\varphi = \mathbf{R}(\varphi,0,0)$ [Eq.(5.7a)]. Then, with the notation of Eq.(5.4),

$$\mathbf{R}_\varphi^* = \mathbf{g}(\varphi,0,0) = \begin{pmatrix} e^{-i\varphi/2} & 0 \\ 0 & e^{i\varphi/2} \end{pmatrix}. \tag{5.9}$$

Now $C_\infty = \{\mathbf{R}_\varphi | 0 \leq \varphi < 2\pi\}$, so

$$C_\infty^* = \{\mathbf{R}_\varphi^* \mid 0 \le \varphi < 2\pi\} \cup \{-\mathbf{R}_\varphi^* \mid 0 \le \varphi < 2\pi\}$$

$$= \{\begin{pmatrix} e^{-i\varphi/2} & 0 \\ 0 & e^{i\varphi/2} \end{pmatrix} \mid 0 \le \varphi < 2\pi\} \cup \{\begin{pmatrix} e^{-i(\varphi/2+\pi)} & 0 \\ 0 & e^{i(\varphi/2+\pi)} \end{pmatrix} \mid 0 \le \varphi < 2\pi\}$$

$$= \{\begin{pmatrix} e^{-i\alpha} & 0 \\ 0 & e^{i\alpha} \end{pmatrix} \mid 0 \le \alpha < 2\pi\}, \qquad (5.10)$$

which is evidently isomorphic to $C_\infty$ itself, that is, we have established that

$$C_\infty^* \simeq C_\infty. \qquad (5.11)$$

If n is a natural number, we have $C_n = \{\mathbf{R}_\varphi \mid \varphi = p2\pi/n;$ $p = 0,1,\ldots,n-1\}$ and one may analogously compute $C_n^*$ to be

$$C_n^* = \{\begin{pmatrix} e^{-i\alpha} & 0 \\ 0 & e^{i\alpha} \end{pmatrix} \mid \alpha = p2\pi/2n;\ p = 0,1,\ldots,2n-1\} \qquad (5.12)$$

so that

$$C_n^* \simeq C_{2n}. \qquad (5.13)$$

## 5.4. Basics of the representation theory of the double groups.

Information on the irreducible representations of the double groups may of course be obtained from character tables as those referred to above (Section 5.1). In [23] we give explicit irreducible matrix representations for all non-commutative double groups, adapted to various group-subgroup hierarchies (given mostly by writing the matrix representatives for a generating set of group elements); [18b] gives irreducible matrix representations in full for the particular case of the double group $D_6^*$.

We shall, however, find it convenient to give a few basic facts in this section. These are all easily derived from the definition of double groups.

We discuss here just the case of a group $G \subseteq SO(3)$ and its double group $G^* \subseteq SU(2)$.

The irreducible representations of $G^*$ may be divided into two classes: (1) those which map $\mathbf{1} \in G^*$ as well as $-\mathbf{1} \in G^*$ to the unit matrix (and which thus assign the same matrix representative to $\mathbf{g}$ and to $-\mathbf{g}$ for all $\mathbf{g} \in G^*$); and (2) those which assign different matrix representatives to $\mathbf{1}$ and $-\mathbf{1}$ (and which actually then assign opposite matrix representatives to $\mathbf{g}$ and $-\mathbf{g}$ for all $\mathbf{g} \in G^*$). The irreducible representations of type (1) are called ordinary or vector or tensor representations*) of $G^*$, while those of class (2)

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*) In view of the fact that a vector representation $\Gamma$ then has the property $\Gamma(-\mathbf{g}) = \Gamma(\mathbf{g})$ for all $\mathbf{g} \in G^*$ and a spin representation $\Gamma$ the property $\Gamma(-\mathbf{g}) = -\Gamma(\mathbf{g})$ for all $\mathbf{g} \in G^*$, it does not seem unreasonable to call vector representations even representations and spin representations odd representations as is done in [13, p.101] and [14, p.162]. However, in view of the fact that these terms have been used in connection with a quite different classification [41], we have chosen not to emphasize them in the main text here.

Another point is that the definition of spin representations might seem to imply that such representations are faithful (injective). That this is not necessarily the case can be seen by studying Table A8 in [6, App.2] (the irrep E''' of $D_6^*$ is not faithful).

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are called extra or spin or spinor representations*) of $G^*$. A vector irreducible representation $\Gamma^*$ of $G^*$ corresponds to an irreducible representation $\Gamma$ of G by

$$\Gamma^*(\mathbf{g}) = \Gamma(\pi(\mathbf{g})) \qquad \text{for} \quad \mathbf{g} \in G^*. \tag{5.14}$$

In fact, all irreducible representations of G arise in this way. For spin irreducible representations $\Gamma^*$ of $G^*$ there are no corresponding representations $\Gamma$ of G satisfying (5.14). These observations justify the terms 'ordinary' and 'extra'.

For the group SU(2) itself, the irreducible representations are $D_j$ with $j = 0, 1/2, 1, 3/2, \ldots$ and $\dim D_j = 2j + 1$ (the dimension of $D_j$); those $D_j$ with $j = 0, 1, 2, \ldots$ are of vector type, while those with $j = 1/2, 3/2, 5/2, \ldots$ are of spin type [4, Sec.5.1; 7, Chap.7; 14, Chap.15]. For $j = 1/2$, one can in particular choose the matrix form

$$\mathfrak{D}^{[\frac{1}{2}]}(\varphi,\theta,\psi) = \mathbf{g}(\varphi,\theta,\psi) \tag{5.15}$$

with $\mathbf{g}(\varphi,\theta,\psi)$ defined in (5.4). With this definition, $\mathfrak{D}^{[\frac{1}{2}]}$ is the so-called contrastandard from of $D_{1/2}$ [36]. The representations $\boldsymbol{\pi}$ and $\pi$ in Chapter 4 are of course equivalent to $D_{1/2}$.

As for notation for the irreducible representations of the rest of the double groups, we refer to the character tables mentioned in Section 5.1 and to [23]. For double groups of class (2) [see end of Chapter 4], which are of the type $G_o^* \times S_2$, it would seem natural to use the subscripts 'u' (ungerade) and 'g' (gerade) in connection with the symbols for the irreducibles of $G_o^*$, parallel to the convention for $G = G_o \times S_2$ itself.

## 6. Using the double groups in ligand field theory.

The developments in Chapter 4 led to the definition of double groups as symmetry groups for Hamiltonians of the form (3.6). To act as such, the double groups - themselves defined as summarized in items (1)-(3) in Chapter 4 - are represented on the space $(V_0 \otimes \mathbb{C}^2)^{\otimes N}$, introduced in Chapter 3, by means of the operator representation $[(\mathcal{P}\circ\eta) \otimes (\Pi\circ\xi)]^{\otimes N}$ (cf. (4.10)).

In the present chapter, we shall illustrate this construction by discussing how double groups are used at the qualitative level in ligand-field theory (cf. Remark $3^0$ at the end of Chapter 4). We are not aiming at the derivation of any new results here; rather, we want to explain, using notation and terminology from the preceding chapters, the mathematics underlying a well-known application of these groups and concepts related to this application (such as Russell-Saunders and jj coupling).

> We consider it outside the scope of these notes to deal with any specific calculations involving spin-orbit coupling. What we hope is that the reader may end up having the feeling of being on firm ground with respect to concepts and definitions when he reads the literature concerned with concrete applications of double groups.

We start again by considering the operator $\mathcal{H}_0$. Chapter 4 suggests as a symmetry group for $\mathcal{H}_0$ the pair $(O(3)^*, [(\mathcal{P}\circ\eta) \otimes (\Pi\circ\xi)]^{\otimes N})$, where $O(3)^* = SU(2) \times S_2$. In fact, however, since the action of $\mathcal{H}_0$ in the spin space is trivial, we may enlarge the symmetry group to the direct product $(O(3)^* \times O(3)^*, [(\mathcal{P}\circ\eta) \otimes (\Pi\circ\xi)]^{\otimes N})$, where the action of the group on the Hilbert space now is the outer tensor product, that is,

$$[(\mathcal{P}\circ\eta)\otimes(\Pi\circ\xi)]^{\otimes N}(g_1,g_2) = [(\mathcal{P}\circ\eta(g_1))\otimes(\Pi\circ\xi(g_2))]^{\otimes N}$$
$$\text{for all } g_1,g_2 \in O(3)^*. \qquad (6.1)$$

If we add the term $\mathcal{V}$ with point group symmetry $G \subseteq O(3)$ to $\mathcal{H}_0$, the group $O(3)^* \times O(3)^*$ with the above representation is not a symmetry group any more, but the group $G^* \times O(3)^*$ is. Adding the spin-orbit coupling term lowers the symmetry still further not only to $G^* \times G^*$, but to the diagonal subgroup $G^* \boxtimes G^* = \{(g,g)\,|\,g \in G^*\}$ (because the elements $g_1$ and $g_2$ in (6.1) now have to coincide to make the scalar product $\mathbf{l}\cdot\mathbf{s}$ transform totally symmetrically). The group $G^* \boxtimes G^*$ is clearly isomorphic to G. If we instead add first the spin-orbit coupling, we get at this intermediate level the symmetry group $O(3)^* \boxtimes O(3)^* = \{(g,g)\,|\,g \in O(3)^*\} \simeq O(3)^*$; subsequent addition of $\mathcal{V}$ then reduces the symmetry to $G^* \boxtimes G^*$, as before. We can summarize these hierarchial relations in the diagram

$$\mathcal{H}_0$$
$$(O(3)^* \times O(3)^*,\ [(\mathcal{P}\circ\eta)\otimes(\Pi\circ\xi)]^{\otimes N})$$

$$\swarrow +\mathcal{V} \qquad\qquad + \sum_{i=1}^{N} \zeta_i \mathbf{l}_i\cdot\mathbf{s}_i \searrow$$

$$G^* \times O(3)^* \qquad\qquad O(3)^* \boxtimes O(3)^* \simeq O(3)^* \qquad (6.2a)$$

$$\searrow + \sum_{i=1}^{N} \zeta_i \mathbf{l}_i\cdot\mathbf{s}_i \qquad\qquad +\mathcal{V} \swarrow$$

$$G^* \boxtimes G^* \simeq G^*$$
$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} + \sum_{i=1}^{N} \zeta_i \mathbf{l}_i\cdot\mathbf{s}_i$$

or, if we disregard improper rotations (so that now $G \subseteq SO(3)$) and furthermore just write the <u>groups</u> involved:

$$\begin{array}{ccc} & SU(2) \times SU(2) & \\ \swarrow & & \searrow \\ G^{*} \times SU(2) & & SU(2) \boxtimes SU(2) \simeq SU(2) \\ \searrow & & \swarrow \\ & G^{*} \boxtimes G^{*} \simeq G^{*} & \end{array} \qquad (6.2b)$$

When analysing a system with respect to the group $SU(2) \times SU(2)$, whether it is a symmetry group or not, one has to decompose the representation $[(\mathcal{P} \circ \eta) \otimes (\Pi \circ \xi)]^{\otimes N}$ into irreducible representations. Irreducible representations of $SU(2) \times SU(2)$ are (see, <u>e.g.</u>, [7, Corollary 6.2]) of the form $D_L \otimes D_S$, where L and S may take on values 0, 1/2, 1, 3/2, ... (cf. end of Sec.5.4). A subspace of V transforming as $D_L \otimes D_S$ is usually designated ${}^{2S+1}L$ or ${}^{2S+1}D_L$ and is called a <u>multiplet</u> [the dimension of ${}^{2S+1}L$ is $\dim D_L \dim D_S = (2L+1)(2S+1)$]. If the decomposition of V into multiplets is achieved by regarding $[(\mathcal{P} \circ \eta) \otimes (\Pi \circ \xi)]^{\otimes N}$ as $[(\mathcal{P} \circ \eta) \otimes \mathcal{J}]^{\otimes N} \otimes [\mathcal{J} \otimes (\Pi \circ \xi)]^{\otimes N}$, where $\mathcal{J}$ in both cases denotes the identity operator, and decomposing the first factor into irreducibles $D_L$ and the second factor into irreducibles $D_S$, the scheme is called L-S <u>coupling</u> or <u>Russell-Saunders</u> <u>coupling</u>.

An actual "coupling" takes place when one subduces the $D_L \otimes D_S$ to $SU(2) \boxtimes SU(2)$, obtaining as usual

$$D_L \otimes D_S = \bigoplus_{J = |L-S|}^{L+S} D_J \, . \qquad (6.3)$$

The total resulting decomposition of V into subspaces transforming as $D_J$-representations of $SU(2) \boxtimes SU(2)$ may be obtained also by decomposing $[(\mathcal{P}\circ\pi)\otimes(\Pi\circ\xi)]$ into irreducible representations $D_j$ of $SU(2)\boxtimes SU(2)$ and then forming the various N-fold tensor products of these. This is the j-j <u>coupling</u> <u>scheme</u>.

When $\mathcal{V}$ is present in the Hamiltonian, we get the situation represented in the lower left of diagram (6.2b). Irreducible representations of $G^* \times SU(2)$ are of the form $\Gamma \otimes D_S$, where $\Gamma$ is an irreducible representation of $G^*$; multiplets are written $^{2S+1}\Gamma$. Upon subduction to $G^* \boxtimes G^*$, the direct product $\Gamma \otimes (D_S \downarrow G^*)$ is decomposed into irreducible representations of $G^*$ (here $D_S \downarrow G^*$ means the restriction of $D_S$ to $G^*$).

<u>Example</u>. By way of illustration, let us consider a system describable as "a single $d$ electron in octahedral symmetry". This means that N=1 and that $V_0$ is a five-dimensional space transforming under the representation $\mathcal{P}$ of SO(3) (or $\mathcal{P}\circ\pi$ of SU(2)) as $D_2$ and, finally, that G = O, the octahedral group. Since $\Pi$, as noted at the end of Sec.5.4, is equivalent to $D_{1/2}$, the SU(2) $\times$ SU(2) multiplet characterization is $^2D$, where D is the spectroscopic abbreviation for $D_2$. If we follow this multiplet down through the diagram (6.2b), we get

$$\begin{array}{ccc} & {}^2D\ (\text{i.e. } D_2 \otimes D_{1/2}) & \\ \swarrow & & \searrow \\ {}^2T_2 \oplus {}^2E & & D_{3/2} \oplus D_{5/2} \\ \searrow & & \swarrow \\ & E'' \oplus U' \oplus U' & \end{array} \qquad (6.4)$$

In (6.4), we have used Griffith's notation for the irreducible representations of $O^*$ (see [6,App.2], where also the correspondence with Bethe's notation [1] is given). The last line may be obtained from <u>either</u> the subduction formulae

$$D_{3/2}(SU(2)) \to U'(O^*)$$
$$D_{5/2}(SU(2)) \to E'' \oplus U'(O^*) \qquad (6.5)$$

<u>or</u> the fact that $D_{1/2}(SU(2)) \to E'(O^*)$ combined with the tensor product relations

$$T_2 \otimes (D_{1/2} \downarrow O^*) = T_2 \otimes E' = E'' \oplus U'$$
$$E \otimes (D_{1/2} \downarrow O^*) = E \otimes E' = U' \qquad (6.6)$$

in $O^*$.

The reader may now compare (6.4) with the discussion of the same kind of system in any standard text (<u>e.g.</u>, [33, Fig.6-1]).

We have an important final remark concerning the application of double groups as presented here. Suppose $G \subseteq SO(3)$. Then for all $g \in G^* \subseteq SU(2)$ we have

$$\begin{aligned}[(\mathcal{P} \circ \eta) \otimes (\Pi \circ \xi)]^{\otimes N}(-\mathbf{g}) &= [\mathcal{P}(\pi(-\mathbf{g})) \otimes \Pi(-\mathbf{g})]^{\otimes N} \\ &= [\mathcal{P}(\pi(\mathbf{g})) \otimes (-\Pi(\mathbf{g}))]^{\otimes N} \qquad (6.7) \\ &= (-1)^N [(\mathcal{P} \circ \eta) \otimes (\Pi \circ \xi)]^{\otimes N}(\mathbf{g}).\end{aligned}$$

This shows that if N is <u>odd</u>, only irreducible representations of <u>spin type</u> of $G^*$ occur in the decomposition of V under the action of $[(\mathcal{P} \circ \eta) \otimes (\Pi \circ \xi)]^{\otimes N}$; if N is <u>even</u>, only vector representations occur (Sec.5.4). Since the latter representations are those which can be factorized through G, <u>i.e.</u>, which correspond to representations of G through the prescription (5.14), one <u>may</u> for even N think of the analysis as performed in terms of G instead of $G^*$.

## 7. **Concluding remarks; comments on the literature.**

To summarize, we have demonstrated that within the framework set up in Chapter 2 regarding the application of group representations, it is perfectly reasonable to consider the double groups (as well as the point groups) as matrix groups, and we have discussed in detail how to suitably define double groups for proper and improper point groups.

In this way, double groups are groups and thus become just as simple to use as, *e.g.*, the point groups and the symmetric groups; character tables, tensor product tables for irreducible representations and tables for descent in symmetry, calculated once and for all, are available (or the latter tables can be worked out using the character tables) and can be applied to classification of energy levels, derivation of selection rules, *etc.*, just as for other groups.

With respect to literature introducing the double groups for such applications, the references given here do not purport to make up an exhaustive collection; rather the particular exposition chosen here dictated the selection of references. There is general agreement that Bethe's paper [1] represents the first application of double groups. It may be of interest to note, however, that the double groups were known to mathematicians long before 1929. The standard reference from the end of the last century would be Klein's *Ikosaedervorlesungen* [42], but the double groups seem to be traceable at least back to 1878 [43] and probably even further [44]. In 1899 Frobenius gave the character tables for the tetrahedral, octahedral, and icosahedral double groups [45]. The classic by Miller, Blichfeldt and Dickson [46], referred to by Opechowski in another context [2, p.554], also discusses double groups (Chap.X).

The double groups have not ceased to have research interest. Some scattered references to more recent literature [17, 18, 19, 23, 40, 47] may help the interested reader get into this field.

> The double groups (or binary groups, as they are also often called) furnish a rich collection of illustrations of group theory and are often used as examples in the mathematical literature (see, *e.g.*, [48]: the quaternion group, isomorphic to $D_2^*$ (cf. Table 2), pp.115-120, and the tetrahedral double group pp.132-134; [49]: the tetrahedral double group pp.56-58; and [50]). In particular, they have some interesting presentations, *i.e.*, definitions in terms of generators and relations [50].

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Table 1

Double groups for improper point groups G

($G \subseteq O(3)$ but $G \nsubseteq SO(3)$)

| G contains the inversion | | G does not contain the inversion | |
|---|---|---|---|
| $G$ | $G^*$ | $G$ | $G^*$ |
| $S_2 = C_i$ | $C_1^* \times S_2 (\simeq C_2 \times C_2)$ | $C_{1h}$ | $C_2^* (\simeq C_4 \ncong C_2 \times C_2)$ |
| $C_{nh}(n=2,4,6,\ldots)$ | $C_n^* \times S_2 (\simeq C_{2n} \times C_2)$ | $C_{nh}(n=3,5,7,\ldots)$ | $C_{2n}^* (\simeq C_{4n} \ncong C_{2n} \times C_2)$ |
| | | $C_{nv}(n=2,3,4,\ldots)$ | $D_n^*$ |
| $S_n(n=2,6,10,\ldots)$ | $C_{n/2}^* \times S_2 (\simeq C_n \times C_2)$ | $S_n(n=4,8,12,\ldots)$ | $C_n^* (\simeq C_{2n})$ |
| $D_{nh}(n=2,4,6,\ldots)$ | $D_n^* \times S_2$ | $D_{nh}(n=3,5,7,\ldots)$ | $D_{2n}^*$ |
| $D_{nd}(n=3,5,7,\ldots)$ | $D_n^* \times S_2$ | $D_{nd}(n=2,4,6,\ldots)$ | $D_{2n}^*$ |
| $T_h$ | $T^* \times S_2$ | $T_d$ | $O^*$ |
| $O_h$ | $O^* \times S_2$ | | |
| $I_h$ | $I^* \times S_2$ | | |
| | | $C_{\infty v}$ | $D_\infty^*$ |
| $D_{\infty h}$ | $D_\infty^* \times S_2$ | | |
| $O(3)$ | $SU(2) \times S_2$ | | |

The fact that $C_n^* \simeq C_{2n}$ (the sign $\simeq$ meaning "is isomorphic to") is proved in Sec.5.3. Note that isomorphic point groups may have non-isomorphic double groups ($S_2$ vs. $C_{1h}$; $C_{2h}$ vs. $C_{2v}$ [$D_2^*$ is not isomorphic to $C_4 \times C_2$, cf. Table 2 below]; $S_n$ vs. $C_n$ for $n = 2,6,10,\ldots$).

Table 2

The dihedral group $D_2$ and its double group $D_2^*$

Elements: $D_2 = \{ \mathbf{E}, \mathbf{C}_2^X, \mathbf{C}_2^Y, \mathbf{C}_2^Z \}$

$= \{ \mathbf{R}(0,0,0), \mathbf{R}(\pi,\pi,0), \mathbf{R}(0,\pi,0), \mathbf{R}(\pi,0,0) \};$

$D_2^* = \{ \mathbf{1}, -\mathbf{1}, \mathbf{C}_2^{X^*}, -\mathbf{C}_2^{X^*}, \mathbf{C}_2^{Y^*}, -\mathbf{C}_2^{Y^*}, \mathbf{C}_2^{Z^*}, -\mathbf{C}_2^{Z^*} \}$

$= \{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}, \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}, \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} \}.$

Character tables:

| $D_2^*$ | $\{\mathbf{1}\}$ | $\{-\mathbf{1}\}$ | $\{\mathbf{C}_2^{X^*}, -\mathbf{C}_2^{X^*}\}$ | $\{\mathbf{C}_2^{Y^*}, -\mathbf{C}_2^{Y^*}\}$ | $\{\mathbf{C}_2^{Z^*}, -\mathbf{C}_2^{Z^*}\}$ |
|---|---|---|---|---|---|
| A | 1 | 1 | 1 | 1 | 1 |
| $B_1$ | 1 | 1 | -1 | -1 | 1 |
| $B_2$ | 1 | 1 | -1 | 1 | -1 |
| $B_3$ | 1 | 1 | 1 | -1 | -1 |
| E' | 2 | -2 | 0 | 0 | 0 |

| $D_4$ | $\{\mathbf{E}\}$ | $\{\mathbf{C}_2^Z\}$ | $\{\mathbf{C}_2^{X=Y}, \mathbf{C}_2^{X=-Y}\}$ | $\{\mathbf{C}_2^X, \mathbf{C}_2^Y\}$ | $\{\mathbf{C}_4^Z, (\mathbf{C}_4^Z)^{-1}\}$ |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | -1 | -1 | 1 |
| $B_1$ | 1 | 1 | -1 | 1 | -1 |
| $B_2$ | 1 | 1 | 1 | -1 | -1 |
| E | 2 | -2 | 0 | 0 | 0 |

---

The elements of $D_2^*$ are computed by formula (5.4) from the Euler angles chosen for the elements of $D_2$ and are named according to the convention in Sec.5.3. Note that changing Euler angles for a given element of the point group may lead to the opposite notation for the two corresponding double group elements, e.g., if we regard $C_2^X$ as $\mathbf{R}(0,\pi,\pi)$, then

$\mathbf{C}_2^{X^*}$ is $\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$ and $-\mathbf{C}_2^{X^*}$ is $\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$, whereas if $\mathbf{C}_2^X$ is regarded as $\mathbf{R}(\pi,\pi,0)$, then

$$\mathbf{C}_2^{X^*} \text{ is } \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} \text{ and } -\mathbf{C}_2^{X^*} \text{ is } \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}.$$

In the character tables, the notation of Griffith [6, App.2] is used.

The character table of the point group $D_4$ is appended to show the interesting fact that non-isomorphic groups may have (in the obvious sense of this expression) the same character table (to see that $D_2^*$ and $D_4$ are not isomorphic, note, for example, that $D_2^*$ has only one element of order 2, namely $-\mathbf{1}$, whereas $D_4$ has 5 such elements). (The problem of determining which groups are characterized by their character tables has intrigued mathematicians; see, e.g., [51].)

## Appendix A. **Transformation properties of the angular momentum operators.**

The purpose of this appendix is to provide a rigorous proof of formula (4.3). (The present author has never seen such a proof in the literature making use of this formula.) Apart from being of interest in its own, such a derivation might serve as a starting point if one wanted to set up formal proofs also in the more general cases discussed in Remark $3^{o}$ at the end of Chapter 4.

For an arbitrary function $\psi$ of the variable $\mathbf{r} = (x,y,z)$, we shall denote by $\psi'_x$ $\psi'_y$, and $\psi'_z$ the three partial derivates of $\psi$; that is,

$$\psi'_x(x,y,z) = \frac{\partial}{\partial x}(\psi(x,y,z)), \ \underline{\text{etc}}.$$

We shall verify that for any element

$$\mathbf{R} = \begin{pmatrix} \mathbf{R}_{xx} & \mathbf{R}_{xy} & \mathbf{R}_{xz} \\ \mathbf{R}_{yx} & \mathbf{R}_{yy} & \mathbf{R}_{yz} \\ \mathbf{R}_{zx} & \mathbf{R}_{zy} & \mathbf{R}_{zz} \end{pmatrix} \in O(3) \tag{A.1}$$

and any function $\psi$ we have

$$[\mathcal{P}(\mathbf{R})\boldsymbol{\ell}_x\mathcal{P}(\mathbf{R})^{-1}]\psi = [\det\mathbf{R}(\mathbf{R}_{xx}\boldsymbol{\ell}_x + \mathbf{R}_{yx}\boldsymbol{\ell}_y + \mathbf{R}_{zx}\boldsymbol{\ell}_z)]\psi; \tag{A.2}$$

in this way we shall have proved formula (4.4), and the proofs of the two other formulae embodied in (4.3) are of course analogous.

We start by calculating, by the chain rule:

$$\forall \mathbf{r} \; : \frac{\partial}{\partial z}[\psi(\mathbf{Rr})] = \psi_x'(\mathbf{Rr})\frac{\partial}{\partial z}\;(\mathbf{R}_{xx}x + \mathbf{R}_{xy}y + \mathbf{R}_{xz}z)$$
$$+ \;\psi_y'(\mathbf{Rr})\frac{\partial}{\partial z}\;(\mathbf{R}_{yx}x + \mathbf{R}_{yy}y + \mathbf{R}_{yz}z)$$
$$+ \;\psi_z'(\mathbf{Rr})\frac{\partial}{\partial z}\;(\mathbf{R}_{zx}x + \mathbf{R}_{zy}y + \mathbf{R}_{zz}z)$$
$$= \sum_{i=x,y,z} \mathbf{R}_{iz}\,\psi_i'(\mathbf{Rr}); \qquad (A.3)$$

similarly, one obtains

$$\forall \mathbf{r} \; : \frac{\partial}{\partial y}[\psi(\mathbf{Rr})] = \sum_{j=x,y,z} \mathbf{R}_{jy}\psi_j'(\mathbf{Rr}). \qquad (A.4)$$

Making use of these formulae, we get (starting with the left-hand side of (A.2)):

$$\forall \mathbf{r} \; : \; [\mathcal{P}(\mathrm{R})\boldsymbol{\ell}_x\mathcal{P}(\mathrm{R}^{-1})]\psi(\mathbf{r})$$
$$= [\mathcal{P}(\mathrm{R})(-i)(y\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y})]\psi(\mathbf{Rr})$$
$$= -i\,[\mathcal{P}(\mathrm{R})(y \sum_{i=x,y,z} \mathbf{R}_{iz}\psi_i' - z \sum_{j=x,y,z} \mathbf{R}_{jy}\psi_j')](\mathbf{Rr})$$
$$= -i\,[\det\mathbf{R}(\mathbf{R}_{xy}x + \mathbf{R}_{yy}y + \mathbf{R}_{zy}z) \sum_{i=x,y,z} \mathbf{R}_{iz}\psi_i'$$
$$-\det\mathbf{R}(\mathbf{R}_{xz}x + \mathbf{R}_{yz}y + \mathbf{R}_{zz}z) \sum_{j=x,y,z} \mathbf{R}_{jy}\psi_j'](\mathbf{r}); \qquad (A.5)$$

here we used that

$$\mathbf{R}^{-1} = (\det\mathbf{R})\mathbf{R}^{\mathsf{T}}, \qquad (A.6)$$

where $^{\mathsf{T}}$ denotes matrix transposition, so that $\mathcal{P}(\mathbf{R})y = \det\mathbf{R}(\mathbf{R}_{xy}x + \mathbf{R}_{yy}y + \mathbf{R}_{zy}z)$ and analogously for $\mathcal{P}(\mathbf{R})z$. Multiplying out the last expression in (A.5) gives 18 terms; collecting these gives

$$(-i)(\det\mathbf{R})\Bigg[\left(0\cdot x - \begin{vmatrix}\mathbf{R}_{xy} & \mathbf{R}_{xz}\\ \mathbf{R}_{yy} & \mathbf{R}_{yz}\end{vmatrix} y - \begin{vmatrix}\mathbf{R}_{xy} & \mathbf{R}_{xz}\\ \mathbf{R}_{zy} & \mathbf{R}_{zz}\end{vmatrix} z\right)\psi'_x$$

$$+ \left(\begin{vmatrix}\mathbf{R}_{xy} & \mathbf{R}_{xz}\\ \mathbf{R}_{yy} & \mathbf{R}_{yz}\end{vmatrix} x + 0\cdot y - \begin{vmatrix}\mathbf{R}_{yy} & \mathbf{R}_{yz}\\ \mathbf{R}_{zy} & \mathbf{R}_{zz}\end{vmatrix} z\right)\psi'_y$$

$$+ \left(\begin{vmatrix}\mathbf{R}_{xy} & \mathbf{R}_{xz}\\ \mathbf{R}_{zy} & \mathbf{R}_{zz}\end{vmatrix} x + \begin{vmatrix}\mathbf{R}_{yy} & \mathbf{R}_{yz}\\ \mathbf{R}_{zy} & \mathbf{R}_{zz}\end{vmatrix} y - 0\cdot z\right)\psi'_z\Bigg](\mathbf{r}); \qquad (A.7)$$

using again (A.6) and the general formula for the inverse of a matrix, (A.7) may further be rewritten as

$$(-i)(\det\mathbf{R})[(-\mathbf{R}_{zx}y + \mathbf{R}_{yx}z)\psi'_x$$
$$+ (\mathbf{R}_{zx}x - \mathbf{R}_{xx}z)\psi'_y$$
$$+ (-\mathbf{R}_{yx}x + \mathbf{R}_{xx}y)\psi'_z](\mathbf{r})$$
$$= (-i)(\det\mathbf{R})[\mathbf{R}_{xx}(y\,\psi'_z - z\,\psi'_y)$$
$$+ \mathbf{R}_{yx}(z\,\psi'_x - x\,\psi'_z)$$
$$+ \mathbf{R}_{zx}(x\,\psi'_y - y\,\psi'_x)](\mathbf{r}); \qquad (A.8)$$

clearly, the last expression in (A.8) is equal to the right-hand side of (A.2), taken at **r**. Thus the proof is completed.

## Appendix B. **A general observation concerning operator "scalar products".**

The spin-orbit coupling operator defined in (3.11) and investigated in Chapter 4 is a special case of what one might call operator "scalar products". The symmetry result we need in Chapter 4 follows from the general discussion we shall give in this appendix.

Suppose we have two Hilbert spaces $V_1$ and $V_2$ and a group G with unitary operator representations $\mathcal{T}_1$ of G on $V_1$ and $\mathcal{T}_2$ of G on $V_2$ (see Chapter 2 regarding the concept of operator representations). Furthermore, let $\Gamma$ be a not necessarily irreducible unitary matrix representation of dimension d of G.

Assume then that we have a set $\mathbf{X} = (\mathcal{X}_1, \ldots, \mathcal{X}_d)$ of operators on $V_1$ transforming as $\Gamma$ under the operator action of $\mathcal{T}_1$ and a set $\mathbf{Y} = (\mathcal{Y}_1, \ldots, \mathcal{Y}_d)$ of operators on $V_2$ transforming as $\bar{\Gamma}$ (the complex conjugate matrix representation) under the operator action of $\mathcal{T}_2$ (cf. Eq.(2.4)). These assumptions may be expressed as

$$\mathcal{T}_1(R)\mathcal{X}_\gamma\mathcal{T}_1(R)^{-1} = \sum_{\gamma'=1}^{d} \Gamma(R)_{\gamma'\gamma}\mathcal{X}_{\gamma'} \quad \text{for all } R \in G$$

$$\text{for each } \gamma = 1, \ldots, d \qquad \text{(B.1)}$$

and

$$\mathcal{T}_2(R)\mathcal{Y}_\gamma\mathcal{T}_2(R)^{-1} = \sum_{\gamma''=1}^{d} \bar{\Gamma}(R)_{\gamma''\gamma}\mathcal{Y}_{\gamma''} \quad \text{for all } R \in G$$

$$\text{for each } \gamma = 1, \ldots, d. \qquad \text{(B.2)}$$

Under these circumstances the "scalar product" $\mathbf{X}\cdot\mathbf{Y}$, defined as the operator

$$\mathbf{X}\cdot\mathbf{Y} = \mathcal{X}_1 \otimes \mathcal{Y}_1 + \mathcal{X}_2 \otimes \mathcal{Y}_2 - \ldots + \mathcal{X}_d \otimes \mathcal{Y}_d \tag{B.3}$$

acting on $V_1 \otimes V_2$, will transform under the operator action of the product representation $\mathcal{T}_1 \otimes \mathcal{T}_2$ as the totally symmetric irreducible representation of G, i.e.,

$$[\mathcal{T}_1(R) \otimes \mathcal{T}_2(R)]\,(\mathbf{X}\cdot\mathbf{Y})\,[\mathcal{T}_1(R)^{-1} \otimes \mathcal{T}_2(R)^{-1}] = \mathbf{X}\cdot\mathbf{Y} \quad \text{for all } R \in G. \tag{B.4}$$

The assertion may be proved by direct calculation using the unitarity of the matrices $\Gamma(R)$, $R \in G$:

$$\forall R \in G : [\mathcal{T}_1(R) \otimes \mathcal{T}_2(R)]\,(\mathbf{X}\cdot\mathbf{Y})[\mathcal{T}_1(R)^{-1} \otimes \mathcal{T}_2(R)^{-1}]$$

$$= \sum_{\gamma=1}^{d} [\mathcal{T}_1(R)\mathcal{X}_\gamma \mathcal{T}_1(R)^{-1}] \otimes [\mathcal{T}_2(R)\mathcal{Y}_\gamma \mathcal{T}_2(R)^{-1}]$$

$$= \sum_{\gamma=1}^{d} \Big(\sum_{\gamma'=1} \Gamma(R)_{\gamma'\gamma}\mathcal{X}_{\gamma'}\Big) \otimes \Big(\sum_{\gamma''=1} \bar{\Gamma}(R)_{\gamma''\gamma}\mathcal{Y}_{\gamma''}\Big)$$

$$= \sum_{\gamma'=1}^{d} \sum_{\gamma''=1}^{d} \Big(\sum_{\gamma=1}^{d} \Gamma(R)_{\gamma'\gamma}\,\bar{\Gamma}(R)_{\gamma''\gamma}\Big)\mathcal{X}_{\gamma'} \otimes \mathcal{Y}_{\gamma''}$$

$$= \sum_{\gamma'=1}^{d} \sum_{\gamma''=1}^{d} \delta_{\gamma'\gamma''}\mathcal{X}_{\gamma'} \otimes \mathcal{Y}_{\gamma''} = \sum_{\gamma'=1}^{d} \mathcal{X}_{\gamma'} \otimes \mathcal{Y}_{\gamma''}$$

$$= \mathbf{X}\cdot\mathbf{Y}\ .$$

There are various other more or less sophisticated ways in which (B.4) may be proved, possibly enabling a better "understanding" of the result. For example, let $W_1 = \mathrm{span}\{\mathcal{X}_1, \ldots, \mathcal{X}_d\}$ (i.e., the linear space spanned by the operators $\mathcal{X}_\gamma$, $\gamma = 1, \ldots, d$) and $W_2 = \mathrm{span}\{\mathcal{Y}_1, \ldots, \mathcal{Y}_d\}$. If $W_1 \otimes W_2$ is looked upon as the space $\mathbf{M}(d,d)$ of $d \times d$ matrices, the action of $\mathcal{T}_1 \otimes \mathcal{T}_2$ on $W_1 \otimes W_2$ is (see, e.g., [13, p.48]):

$$\forall R \in G: [\mathcal{T}_1(R) \otimes \mathcal{T}_2(R)](\mathbf{W}) = \Gamma(R)\mathbf{W}\,\Gamma(R^{-1})$$

for all $\mathbf{W} \in \mathbf{M}(d,d)$.

Since $\mathbf{X}\cdot\mathbf{Y}$ is represented by the unit matrix in $\mathbf{M}(d,d)$, it is clear that it is a fix-vector under $\mathcal{T}_1 \otimes \mathcal{T}_2$.

The operator $\mathbf{l}\cdot\mathbf{s}$ fits well into the above framework. In Chapter 4 we show that $\mathbf{l}$ transforms under $\mathcal{P}\circ\eta$ as the real unitary matrix representation $\mathbf{D}_1 \downarrow G^*$ (the restriction to $G^*$ of the SU(2)-irrep $\mathbf{D}_1$) and that $\mathbf{s}$ transforms under $\Pi\circ\xi$ as the <u>same</u> representation of $G^*$ (and thus, since $\mathbf{D}_1$ is real, also as $\bar{\mathbf{D}}_1$).

One may rewrite an operator of the form (B.3) by applying a unitary transformation $\mathbf{U}$ leading to linear combinations

$$x'_\gamma = \sum_{\gamma'} \mathbf{U}_{\gamma\gamma'} x_{\gamma'} \tag{B.6}$$

<u>if</u> one transforms the operators $y_\gamma$ by the <u>complex</u> <u>conjugate</u> transformation $\bar{\mathbf{U}}$, since then

$$\sum_\gamma x'_\gamma \otimes y'_\gamma = \sum_\gamma \Big(\sum_{\gamma'} \mathbf{U}_{\gamma\gamma'} x_{\gamma'}\Big) \otimes \Big(\sum_{\gamma''} \bar{\mathbf{U}}_{\gamma\gamma''} y_{\gamma''}\Big)$$

$$= \sum_{\gamma'} \sum_{\gamma''} \Big(\sum_\gamma \mathbf{U}_{\gamma\gamma'} \bar{\mathbf{U}}_{\gamma\gamma''}\Big) x_{\gamma'} \otimes y_{\gamma''}$$

$$= \sum_{\gamma'} \sum_{\gamma''} \delta_{\gamma'\gamma''}\, x_{\gamma'} \otimes y_{\gamma''} = \mathbf{X}\cdot\mathbf{Y}\,.$$

The property that the two operator sets transform by mutually complex conjugate matrix representations is preserved under this kind of transformation. (<u>Formally</u>, the essence of the above is of course just the well-known fact from linear algebra that a unitary transformation preserves scalar products.)

As an example, we may transform $(\ell_x, \ell_y, \ell_z)$ into the set $(\ell_1, \ell_0, \ell_{-1})$ transforming as the contrastandard [36] form $\mathcal{D}^{[1]}$ of the irreducible representation $D_1$ of SU(2) [cf. Sec.5.4] and defined here by

$$\ell_1 = -\frac{\sqrt{2}}{2}(\ell_x + i\,\ell_y)$$
$$\ell_0 = \ell_z \qquad (B.8)$$
$$\ell_{-1} = \frac{\sqrt{2}}{2}(\ell_x - i\,\ell_y)$$

(see formula (9) in [24b]). Using the complex conjugate transformation on the set $(s_x, s_y, s_z)$ gives the set $(-s_{-1}, s_0, -s_1)$ so that the operator $\mathbf{l}\cdot\mathbf{s}$ with these alternative operator bases reads

$$\mathbf{l}\cdot\mathbf{s} = -\ell_1 \otimes s_{-1} + \ell_0 \otimes s_0 - \ell_{-1} \otimes s_1. \qquad (B.9)$$

Finally we wish to point out that it is a convenient thing that we did not assume irreducibility of the representation $\Gamma$ above. The operator sets $\mathbf{l}$ and $\mathbf{s}$ do transform, as we have seen, as the 3-dimensional irreducible representation of SU(2); but descending to a double group $G^* \subseteq SU(2)$, one may well find that the representations spanned by these operator sets are reducible. The occurrence of this phenomenon is of course governed by the subduction relations telling how $D_1(SU(2))$ splits up into subgroup irreducibles when restricted to $G^*$.

## Appendix C.

Any subgroup $G \subseteq O(3)$ which is not a subgroup of $SO(3)$ belongs to exactly one of the following two classes of groups:

(i) The inversion is an element of G, i.e., $-E \in G$. Consider the set $G_0 = G \cap SO(3)$; being the kernel of that homomorphism from G into the multiplicative group $\{1,-1\}$ which maps elements of G into their determinant, $G_0$ is a normal subgroup of G. The set $\{E,-E\}$ is clearly also a normal subgroup of G, and $G_0 \cap \{E,-E\} = \{E\}$. Furthermore, the product $G_0\{E,-E\}$ is all of G, because any element $\mathbf{R} \in G$ is either in $G_0$ or, if not, can be written $(-\mathbf{R})(-E)$ with $-\mathbf{R} \in G$. This proves that $G = G_0 \times \{E,-E\}$.

(ii) The inversion is not an element of G, i.e., $-E \notin G \nsubseteq SO(3)$. Consider the set $G' = \mathbf{D}_1(G) = \{(\det\mathbf{R})\mathbf{R} \mid \mathbf{R} \in G\} \subseteq SO(3)$, where $\mathbf{D}_1$ is the matrix representation defined in Chapter 4. The set G' is a homomorphic image of G, and since

$$\forall \mathbf{R} \in G\colon \mathbf{D}_1(\mathbf{R}) = \mathbf{E} \Rightarrow \mathbf{R} = (\det\mathbf{R})^{-1}\, E = \pm\,\mathbf{E} \Rightarrow \mathbf{R} = \mathbf{E}$$

(because $-E \notin G$), the restriction of $\mathbf{D}_1$ to G is injective and G' is a subgroup of $SO(3)$ isomorphic to G.

Other authors have had occasion to consider other isomorphisms between groups of class (ii) and "pure rotation groups" (SO(3)-subgroups) than those defined by $\mathbf{D}_1$; see [47] and references therein.

Appendix D.

Suppose we consider two different ways of choosing the rotation axes defining a given proper point group (with respect to a fixed coordinate system). We then get the point group represented as two different matrix subgroups $G_1 \subseteq SO(3)$ and $G_2 \subseteq SO(3)$. We ask what the relationship is between the double groups $G_1^*$ and $G_2^*$ as defined in Chapter 4.

Now there will be a rotation $\mathbf{R_o}$ connecting the two orientations of the defining axes of the point group so that $G_1 = \mathbf{R_o} G_2 \mathbf{R_o}^{-1}$ (i.e., $G_1$ and $G_2$ are conjugate subgroups of $SO(3)$). Let $\mathbf{g_o} \in SU(2)$ with $\pi(\mathbf{g_o}) = \mathbf{R_o}$, where $\pi\colon SU(2) \to SO(3)$ is defined by Proposition 2 in Chapter 4. We claim that $G_1^* = \mathbf{g_o} G_2^* \mathbf{g_o}^{-1}$ so that $G_1^*$ and $G_2^*$ are conjugate in $SU(2)$ (and thus, in particular, isomorphic).

For the proof, first note that $\pi(\mathbf{g_o} G_2^* \mathbf{g_o}^{-1}) = \pi(\mathbf{g_o})\pi(G_2^*)\pi(\mathbf{g_o}^{-1}) = \mathbf{R_o} G_2 \mathbf{R_o}^{-1} = G_1$; this implies that $\mathbf{g_o} G_2^* \mathbf{g_o}^{-1} \subseteq G_1^*$. Applying the same argument to $\mathbf{g_o}^{-1} G_1^* \mathbf{g_o}$ gives $\mathbf{g_o}^{-1} G_1^* \mathbf{g_o} \subseteq G_2^*$, using that $\mathbf{R_o}^{-1} G_1 \mathbf{R_o} = G_2$, and thus $G_1^* \subseteq \mathbf{g_o} G_2^* \mathbf{g_o}^{-1}$. In all, we have $\mathbf{g_o} G_2^* \mathbf{g_o}^{-1} = G_1^*$, as desired.

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